

**CONVERTING PROPYLENE IN AN OXYGENATE-CONTAMINATED
PROPYLENE STREAM TO NON-POLYMERIZATION
DERIVATIVE PRODUCTS**

FIELD OF THE INVENTION

[0001] This invention relates to converting products of an oxygenate-to-olefin reaction system to non-polymerization products, and more particularly, to converting propylene in an oxygenate contaminated propylene-containing product stream from an oxygenate-to-olefin reaction system to one or more non-polymerization products.

BACKGROUND OF THE INVENTION

[0002] Light olefins, particularly ethylene and propylene, serve as feeds for the production of numerous important chemicals and polymers. Olefins have been traditionally produced from petroleum feedstock by catalytic or steam cracking processes. These cracking processes, especially steam cracking, produce light olefin(s) such as ethylene and/or propylene from a variety of hydrocarbon feedstock. Ethylene and propylene are important commodity petrochemicals useful in a variety of processes for making plastics and other chemical compounds. Propylene is used to make various polypropylene plastics, and in making other chemicals such as acrylonitrile and propylene oxide. Because of the limited supply and escalating cost of petroleum feeds, the cost of producing olefins from petroleum sources has increased steadily. Efforts to develop and improve olefin production technologies, particularly light olefins production technologies, have increased.

[0003] The petrochemical industry has known for some time that oxygenates, especially alcohols, are convertible into light olefin(s). In an oxygenate to olefin (OTO) reaction system, a feedstock containing an oxygenate is vaporized and introduced into a reactor. Exemplary oxygenates include alcohols such as methanol and ethanol, dimethyl ether, methyl ethyl ether, methyl formate, and dimethyl carbonate. In a methanol to olefin (MTO) reaction system, the oxygenate in the oxygenate-containing feedstock is methanol. In the reactor, the methanol contacts a catalyst under conditions effective to create desirable light olefins, such as propylene. Typically, molecular sieve catalysts have been

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used to convert oxygenate compounds to olefins. Silicoaluminophosphate (SAPO) molecular sieve catalysts are particularly desirable in such conversion processes because they are highly selective in the formation of ethylene and propylene.

[0004] Undesirable C_4+ or C_5+ olefins (heavy olefins) may be formed as byproducts of the OTO process. U.S. Patent No. 5,714,662 to Vora et al. provides a practical use for a C_3 and C_4 olefin stream separated from an MTO product effluent and for water byproduct formed in the MTO process. More specifically, the Vora et al. patent is directed to a process for producing light olefins from crude methanol. The patent discloses that propylene and butylene fractions from the MTO product effluent may be converted to high octane ether and other high value products. Optionally, butylene from the MTO process may be dimerized and hydrogenated to produce a C_8 alkylate having a high octane for use in blending motor gasoline.

[0005] Undesirable oxygenate compounds such as alcohols, aldehydes, ketones, esters, acids and ethers in the C_1 to C_6 range as well as trace quantities of aromatic compounds may also be formed in OTO reactors or in effluent processing. Additionally, a small amount of oxygenate from the feedstock, e.g., methanol or dimethyl ether ("DME"), may pass through the OTO reactor with the product effluent without being converted to desired product. As a result of oxygenate synthesis and/or less than complete/quantitative conversion of the oxygenate feedstock in an OTO reaction system, the effluent from an OTO reactor may contain undesirably high concentrations of oxygenate compounds.

[0006] Oxygenate and heavy olefin compounds contained in an OTO product effluent may be undesirable for several reasons. For example, in order for an olefin-containing effluent to be suitable for catalytic polymerization using a low valence state organometallic (e.g., metallocene) and/or a Ziegler-Natta-type catalyst, the effluent should contain no more than 1-5 ppm of oxygenates. Achieving these low levels of oxygenates is possible using conventional separation technologies (i.e., fractionation, absorption and adsorption), thereby providing an olefin product stream of a sufficient grade for polymerization.

However, increased investment and operating costs are required to separate and recover the oxygenates from the desired polymerization quality light olefins.

[0007] In a typical OTO reaction system, ethylene and propylene streams are readily separable from one another and from a C₄+ product fraction through well known separation techniques. Although the ethylene fraction from an OTO reaction system is relatively pure with respect to oxygenates, a considerable amount of undesirable contaminants are concentrated in the propylene product fraction. The major contaminants in the propylene product fraction are oxygenates such as methanol, ethanol, dimethyl ether (DME), ethanal, propanal, acetone and isopropyl alcohol. These oxygenates have proven expensive to remove from the propylene product fraction. Thus, a need exists for providing end uses for an oxygenate-contaminated propylene product fraction from an OTO reaction system without having to invest in removing the oxygenate contaminants.

SUMMARY OF THE INVENTION

[0008] The present invention provides a practical use for a propylene-containing stream that contains a minor amount of oxygenate contaminants. The invention is particularly suited for an unpurified propylene stream or fraction from an oxygenate-to-olefin (OTO) reaction system, such as a methanol-to-olefin (MTO) reaction system. Applicants have discovered that a variety of derivative non-polymerization reaction processes that require a propylene-containing feedstock are relatively insensitive to the presence of the specific oxygenate contaminants found in an unpurified propylene-containing effluent that is derived from an OTO reaction system. Exemplary reaction processes that can tolerate more than about 1 weight percent oxygenate contaminants in a propylene-containing feedstock include: oxidation to form acrolein, oxidation to form acrylic acid, ammoxidation to form acrylonitrile, liquid phase oxidation to form acetone, liquid phase hydration to form isopropanol, hydroformylation to form n-butylaldehyde and its subsequent aldol/hydrogenation to form 2-ethylhexanol, direct oxidation to form propylene oxide, alkylation to form cumene in the presence of either zeolite or phosphoric acid/Kieselguhr catalysts, and the

subsequent selective hydroperoxidation of cumene to form propylene oxide and phenol.

[0009] In one embodiment, the invention is directed to a process for forming a derivative product from an oxygenate-to-olefin (OTO) reaction system product stream. This inventive process includes a step of providing a product stream from an OTO reaction system. The product stream comprises propylene and one or more oxygenate contaminants such as, for example, methanol, ethanol, dimethyl ether (DME), ethanal, propanal, acetone and/or isopropyl alcohol. The process includes directing the product stream to a derivative process reactor and converting the propylene in the derivative process reactor to the derivative product. The derivative product comprises one or more of acrolein, acrylic acid, acrylonitrile, acetone, isopropanol, cumene, n-butyraldehyde, iso-butyraldehyde, 2-ethyl hexanol or propylene oxide. After the converting, a derivative product effluent comprising the derivative product and at least a portion of the oxygenate contaminants is removed from the derivative process reactor. Preferably, the oxygenate contaminant is removed from the derivative product effluent through distillation or other well-known separation techniques. The product stream optionally comprises at least about 1 wppm, at least about 10 wppm, at least about 1000 wppm, at least about 1 wt %, at least about 2 wt %, at least about 5 wt %, at least about 10 wt %, less than about 10 wt %, or from about 10 wppm to about 10 wt % oxygenate contaminants, based on the total weight of the product stream.

[0010] Another embodiment of the invention provides a process for forming a product from a propylene-containing stream, including providing a propylene-containing stream from an oxygenate to olefin reaction system, and contacting propylene in the propylene-containing stream with a catalyst under conditions effective to form the product. The propylene-containing stream comprises at least about 1 wppm, at least about 10 wppm, at least about 1000 wppm, at least about 1 wt %, at least about 2 wt %, at least about 5 wt %, at least about 10 wt %, less than about 10 wt %, or from about 10 wppm to about 10 wt % oxygenate contaminants, based on the total weight of the propylene-containing stream. The oxygenate contaminants comprise one or more of the following: methanol, ethanol, dimethyl ether (DME), ethanal, propanal, acetone, isopropyl

alcohol and/or a mixture thereof. A derivative product effluent comprising the derivative product and the oxygenate contaminant optionally is directed to a separation unit wherein at least a portion of the oxygenate contaminants are removed from the derivative product effluent.

[0011] Optionally, the product is selected from the group consisting of acrolein, acrylic acid, acrylonitrile, acetone, isopropanol, cumene, n-butyraldehyde, iso-butyraldehyde, 2-ethyl hexanol, and propylene oxide. Optionally, the product comprises acrolein, and the catalyst is a complex oxide based upon molybdenum and bismuth in combination with one or more of cobalt, iron, phosphorous or nickel. Alternatively, the product comprises acrylic acid, and the catalyst comprises an oxide of a metal selected from the group consisting of molybdenum, vanadium optionally with one or more of tungsten, copper, iron or manganese. Alternatively, the product comprises acrylonitrile, and the catalyst comprises an oxidic structure of the bismuth molybdate or bismuth ferromolybdate types. Alternatively, the product comprises acetone, and the catalyst comprises $\text{PdCl}_2 \cdot \text{CuCl} \cdot \text{H}_2\text{O}$. Alternatively, the product comprises isopropanol and the catalyst is selected from the group consisting of sodium silicotungstate, an ion exchange resin and sulphuric acid. Alternatively, the product comprises cumene and the catalyst is selected from the group consisting of phosphoric acid/Kieselguhr or a zeolite. Alternatively, the product comprises 2-ethylhexanol and the catalyst comprises a cobalt carbonyl salt, which optionally comprises a phosphine ligand complex. The phosphine ligand complex optionally comprises a rhodium phosphine ligand complex. Alternatively, the product comprises propylene oxide and the catalyst comprises a molybdenum complex in solution. The process optionally further comprises the step of separating a majority of the oxygenate contaminants from the product.

BRIEF DESCRIPTION OF THE DRAWING

[0012] This invention will be better understood by reference to the Detailed Description of the Invention when taken together with the attached drawing, wherein:

Fig. 1 illustrates an oxygenate to olefin reaction system and a reaction effluent separation system; and

Fig. 2 illustrates an oxygenate to olefin reaction system and a reaction effluent separation system.

DETAILED DESCRIPTION OF THE INVENTION

Introduction

[0013] The present invention provides practical uses for propylene-containing streams that contain minor amounts of oxygenate contaminants. The invention is particularly well-suited for an unpurified propylene stream derived from an oxygenate-to-olefin (OTO) reaction system and, particularly, from a methanol-to-olefin (MTO) reaction system. Since the propylene-containing stream may contain a minor amount of oxygenate contaminants, the product separation sequence in an OTO reaction system can be advantageously simplified, and a commensurate decrease in start-up and operating costs can be realized.

[0014] An unpurified propylene-containing stream derived from an OTO reaction system can, depending on reaction conditions and any upstream effluent processing, contain a minor amount of oxygenate contaminants such as methanol, ethanol, dimethyl ether (DME), ethanal, propanal, acetone, isopropyl alcohol or a mixture thereof. It has now been discovered that several non-polymerization derivative processes that require propylene-containing feedstocks are relatively insensitive to the presence of these oxygenate contaminants. Specifically, the catalysts implemented in these non-polymerization derivative reaction processes are relatively insensitive to the oxygenate contaminants contained in an unpurified propylene-containing fraction from an OTO reaction system. As a result, an unpurified propylene-containing fraction from an OTO reaction system may be directed to a non-polymerization derivative reactor for conversion of the propylene contained therein to one or more non-polymerization derivative products. As used herein, an “unpurified” or “contaminated” stream means a stream containing at least about 1 wppm, optionally at least about 5 wppm, or optionally at least about 10 wppm oxygenate contaminants, based on the total weight of the stream.

[0015] A non-limiting list of exemplary derivative non-polymerization propylene conversion processes that can tolerate a propylene-containing feedstock containing a minor amount of oxygenate contaminants includes: oxidation to form acrolein, oxidation to form acrylic acid, ammoxidation to form acrylonitrile, liquid phase oxidation to form acetone, liquid phase hydration to form isopropanol, hydroformylation to form n-butyraldehyde and its subsequent aldol/hydrogenation to form 2-ethylhexanol, direct oxidation to form propylene oxide, alkylation to form cumene in the presence of either zeolite or phosphoric acid/Kieselguhr catalysts, and the subsequent selective hydroperoxidation of cumene to form propylene oxide and phenol. Thus, the unpurified propylene-containing fraction from an OTO reaction system is suitable for disposition to these derivative non-polymerization processes. As a result, a significant commercial savings can be realized by not having to yield a purified oxygenate-free stream from an OTO reaction system to a derivative non-polymerization reaction unit. Each of these derivative non-polymerization processes is discussed in more detail below after a detailed description of OTO Reaction systems.

Oxygenate to Olefin Reaction Systems

[0016] As indicated above, the present invention is particularly suited for converting an unpurified propylene-containing stream from an OTO reaction system, which is discussed in more detail hereinafter, to one or more derivative non-polymerization products.

[0017] Typically, molecular sieve catalysts have been used to convert oxygenate compounds to light olefins. Silicoaluminophosphate (SAPO) molecular sieve catalysts are particularly desirable in such conversion processes because they are highly selective in the formation of ethylene and propylene. A non-limiting list of preferable SAPO molecular sieve catalysts includes SAPO-17, SAPO-18, SAPO-34, SAPO-35, SAPO-44, the substituted forms thereof, and mixtures thereof.

[0018] The feedstock preferably contains one or more aliphatic-containing compounds that include alcohols, amines, carbonyl compounds for example aldehydes, ketones and carboxylic acids, ethers, halides, mercaptans, sulfides, and

the like, and mixtures thereof. The aliphatic moiety of the aliphatic-containing compounds typically contains from 1 to about 50 carbon atoms, preferably from 1 to 20 carbon atoms, more preferably from 1 to 10 carbon atoms, and more preferably from 1 to 4 carbon atoms, and most preferably methanol.

[0019] Non-limiting examples of aliphatic-containing compounds include: alcohols such as methanol and ethanol, alkyl-mercaptans such as methyl mercaptan and ethyl mercaptan, alkyl-sulfides such as methyl sulfide, alkyl-amines such as methyl amine, alkyl-ethers such as DME, diethyl ether and methylethyl ether, alkyl-halides such as methyl chloride and ethyl chloride, alkyl ketones such as dimethyl ketone, alkyl-aldehydes such as formaldehyde and acetaldehyde, and various acids such as acetic acid.

[0020] In a preferred embodiment, the feedstock contains one or more oxygenates, more specifically, one or more organic compounds containing at least one oxygen atom. In a most preferred embodiment, the oxygenate in the feedstock is one or more alcohols, preferably aliphatic alcohols where the aliphatic moiety of the alcohol(s) has from 1 to 20 carbon atoms, preferably from 1 to 10 carbon atoms, and most preferably from 1 to 4 carbon atoms. The alcohols useful as feedstock in the process of the invention include lower straight and branched chain aliphatic alcohols and their unsaturated counterparts. Non-limiting examples of oxygenates include methanol, ethanol, n-propanol, isopropanol, methyl ethyl ether, DME, diethyl ether, di-isopropyl ether, formaldehyde, dimethyl carbonate, dimethyl ketone, acetic acid, and mixtures thereof. In the most preferred embodiment, the feedstock is selected from one or more of methanol, ethanol, DME, diethyl ether or a combination thereof, more preferably methanol and DME, and most preferably methanol.

[0021] The various feedstocks discussed above, particularly a feedstock containing an oxygenate, more particularly a feedstock containing an alcohol, is converted primarily into one or more olefins. The olefins or olefin monomers produced from the feedstock typically have from 2 to 30 carbon atoms, preferably 2 to 8 carbon atoms, more preferably 2 to 6 carbon atoms, still more preferably 2 to 4 carbons atoms, and most preferably ethylene and/or propylene.

[0022] Non-limiting examples of olefin monomer(s) include ethylene, propylene, butene-1, pentene-1, 4-methyl-pentene-1, hexene-1, octene-1 and decene-1, preferably ethylene, propylene, butene-1, pentene-1, 4-methyl-pentene-1, hexene-1, octene-1 and isomers thereof. Other olefin monomers include unsaturated monomers, diolefins having 4 to 18 carbon atoms, conjugated or nonconjugated dienes, polyenes, vinyl monomers and cyclic olefins.

[0023] In the most preferred embodiment, the feedstock, preferably of one or more oxygenates, is converted in the presence of a molecular sieve catalyst composition into olefin(s) having 2 to 6 carbons atoms, preferably 2 to 4 carbon atoms. Most preferably, the olefin(s), alone or combination, are converted from a feedstock containing an oxygenate, preferably an alcohol, most preferably methanol, to the preferred olefin(s) ethylene and/or propylene.

[0024] The most preferred process is generally referred to as gas-to-olefins (GTO) or, alternatively, methanol-to-olefins (MTO). In an MTO process, a methanol-containing feedstock is converted in the presence of a molecular sieve catalyst composition into one or more olefins, preferably and predominantly, ethylene and/or propylene, referred to herein as light olefins. Preferably, at least 90 weight percent, more preferably at least 95 weight percent, and most preferably at least 99 weight percent of the methanol in the feedstock is converted to light olefins, based on the total weight of the methanol in the feedstock.

[0025] The feedstock, in one embodiment, contains one or more diluents, typically used to reduce the concentration of the feedstock. The diluents are generally non-reactive to the feedstock or molecular sieve catalyst composition. Non-limiting examples of diluents include helium, argon, nitrogen, carbon monoxide, carbon dioxide, water, essentially non-reactive paraffins (especially alkanes such as methane, ethane, and propane), essentially non-reactive aromatic compounds, and mixtures thereof. The most preferred diluents are water and nitrogen, with water being particularly preferred. In other embodiments, the feedstock does not contain any diluent.

[0026] The diluent may be used either in a liquid or a vapor form, or a combination thereof. The diluent is either added directly to a feedstock entering into a reactor or added directly into a reactor, or added with a molecular sieve

catalyst composition. In one embodiment, the amount of diluent in the feedstock is in the range of from about 1 to about 99 mole percent based on the total number of moles of the feedstock and diluent, preferably from about 1 to 80 mole percent, more preferably from about 5 to about 50, most preferably from about 5 to about 25. In one embodiment, other hydrocarbons are added to a feedstock either directly or indirectly, and include olefin(s), paraffin(s), aromatic(s) (see for example U.S. Patent No. 4,677,242, addition of aromatics) or mixtures thereof, preferably propylene, butylene, pentylene, and other hydrocarbons having 4 or more carbon atoms, or mixtures thereof.

[0027] The process for converting a feedstock, especially a feedstock containing one or more oxygenates, in the presence of a molecular sieve catalyst composition of the invention, is carried out in a reaction process in a reactor, where the process is a fixed bed process, a fluidized bed process (includes a turbulent bed process), preferably a continuous fluidized bed process, and most preferably a continuous high velocity fluidized bed process.

[0028] The reaction processes can take place in a variety of catalytic reactors such as hybrid reactors that have a dense bed or fixed bed reaction zones and/or fast fluidized bed reaction zones coupled together, circulating fluidized bed reactors, riser reactors, and the like. Suitable conventional reactor types are described in for example U.S. Patent No. 4,076,796, U.S. Patent No. 6,287,522 (dual riser), and Fluidization Engineering, D. Kunii and O. Levenspiel, Robert E. Krieger Publishing Company, New York, New York 1977, which are all herein fully incorporated by reference.

[0029] The preferred reactor type is any of the riser reactors generally described in Riser Reactor, Fluidization and Fluid-Particle Systems, pages 48 to 59, F.A. Zenz and D.F. Othmer, Reinhold Publishing Corporation, New York, 1960, and U.S. Patent No. 6,166,282 (fast-fluidized bed reactor), and U.S. Patent Application Serial No. 09/564,613 filed May 4, 2000 (multiple riser reactor), which are all herein fully incorporated by reference.

[0030] In an embodiment, the amount of liquid feedstock fed separately or jointly with a vapor feedstock, to a reaction system is in the range of from 0.1 weight percent to about 85 weight percent, preferably from about 1 weight

percent to about 75 weight percent, more preferably from about 5 weight percent to about 65 weight percent based on the total weight of the feedstock including any diluent contained therein. The liquid and vapor feedstocks are preferably the same composition, or contain varying proportions of the same or different feedstock with the same or different diluent.

[0031] The conversion temperature employed in the conversion process, specifically within the reaction system, is in the range of from about 392°F (200°C) to about 1832°F (1000°C), preferably from about 482°F (250°C) to about 1472°F (800°C), more preferably from about 482°F (250°C) to about 1382°F (750°C), yet more preferably from about 572°F (300°C) to about 1202°F (650°C), yet even more preferably from about 662°F (350°C) to about 1112°F (600°C) most preferably from about 662°F (350°C) to about 1022°F (550°C).

[0032] The conversion pressure employed in the conversion process, specifically within the reaction system, varies over a wide range including autogenous pressure. The conversion pressure is based on the partial pressure of the feedstock exclusive of any diluent therein. Typically the conversion pressure employed in the process is in the range of from about 0.1 kPaa to about 5 MPaa, preferably from about 5 kPaa to about 1 MPaa, and most preferably from about 20 kPaa to about 500 kPaa.

[0033] The weight hourly space velocity (WHSV), particularly in a process for converting a feedstock containing one or more oxygenates in the presence of a molecular sieve catalyst composition within a reaction zone, is defined as the total weight of the feedstock excluding any diluents fed to the reaction zone per hour per weight of molecular sieve in the molecular sieve catalyst composition in the reaction zone. The WHSV is maintained at a level sufficient to keep the catalyst composition in a fluidized state within a reactor.

[0034] Typically, the WHSV ranges from about 1 hr⁻¹ to about 5000 hr⁻¹, preferably from about 2 hr⁻¹ to about 3000 hr⁻¹, more preferably from about 5 hr⁻¹ to about 1500 hr⁻¹, and most preferably from about 10 hr⁻¹ to about 1000 hr⁻¹. In one preferred embodiment, the WHSV is greater than 20 hr⁻¹, preferably the WHSV for conversion of a feedstock containing methanol, DME, or both, is in the range of from about 20 hr⁻¹ to about 300 hr⁻¹.

[0035] The superficial gas velocity (SGV) of the feedstock including diluent and reaction products within the reaction system is preferably sufficient to fluidize the molecular sieve catalyst composition within a reaction zone in the reactor. The SGV in the process, particularly within the reaction system, more particularly within the riser reactor(s), is at least 0.1 meter per second (m/sec), preferably greater than 0.5 m/sec, more preferably greater than 1 m/sec, even more preferably greater than 2 m/sec, yet even more preferably greater than 3 m/sec, and most preferably greater than 4 m/sec. See for example U.S. Patent Application Serial No. 09/708,753 filed November 8, 2000, which is herein incorporated by reference.

[0036] Figure 1 is a flow diagram illustrating an OTO reaction system, generally designated 100, and will now be described in greater detail. An oxygenate containing feedstock or feed stream 120 is fed to a feed vaporization and introduction (FVI) system 121, which subjects the methanol in the methanol-containing feed stream 120 to conditions, e.g., heat and pressure, sufficient to at least partially vaporize the methanol. For example, the FVI system preferably includes a vapor-liquid disengaging drum, in which conditions are sufficient to provide a vaporized methanol-containing stream 122 and a liquid stream, not shown, which may include non-volatiles. The vaporized methanol-containing stream 122 is directed to OTO reactor unit 123, in which the methanol in vaporized methanol-containing stream 122 contacts an OTO catalyst under conditions effective to convert at least a portion of the oxygenates to light olefins in product stream 124. Product stream 124 includes methane, ethylene, ethane, propylene, propane, C4 olefins, C5+ hydrocarbons, other hydrocarbon components, water, and oxygenates such as one or more of DME, methanol, ethanol, ethanal, propanal, acetone, and/or isopropyl alcohol.

[0037] The product stream 124 preferably is then directed to a quench unit 125, e.g., a quench tower, wherein the product stream 124 is cooled and water and other readily condensable components are condensed. The condensed components, which comprise a substantial amount of water, are withdrawn from the quench unit 125 through a quench bottoms stream 139. A portion of the condensed components are circulated through a recirculation line, not shown,

back to the top of the quench unit 125. The recirculation line optionally contains a cooling unit, e.g., a heat exchanger, not shown, to further cool the condensed components so as to provide a cooling medium, e.g., a quench medium, to further cool the components in quench unit 125.

[0038] Olefin vapor leaves through the overhead portion of quench unit 125 through quench overhead line 126. The olefin vapor in quench overhead line 126 is compressed in one or more stages and one or more compressors in compression zone 127 to form a compressed product stream 128. After each of one or more stages, the compressed stream passes through a heat exchanger, not shown, and is cooled in order to condense out heavier components such as residual water. The condensed component(s) are collected in one or more knock out drums, not shown, between compression stages and exit the compression zone 127 via compression condensate stream(s) 140. Compressed product stream 128 optionally passes through a water absorption unit, not shown, where methanol is preferably used as the water absorbent. In the water absorption unit, the water absorbent contacts the compressed product stream 128, preferably in a countercurrent manner, under conditions effective to separate water from the other components in the compressed product stream 128. The light olefins are recovered from the water absorption unit in an overhead stream, not shown. Optionally-washed compressed product stream 128 is directed to a separation system for separating the various components contained therein.

[0039] A variety of separation systems may be implemented in accordance with the present invention so long as the separation system forms a propylene-containing stream suitable for conversion to the one or more non-polymerization derivative products disclosed herein. U.S. Patent Applications Serial Nos. 10/125,138, filed April 18, 2002, and 10/124,859, also filed April 18, 2002, the entireties of which are incorporated herein by reference, describe two separation schemes which may be implemented in accordance with the present invention. Two additional separation systems that may form the contaminated propylene-containing stream for use in the non-polymerization derivative processes are described in U.S. Patent Application Serial No. 10/383,204, which was filed March 6, 2003, and in U.S. Patent Application Serial No. 10/635,410

(methanol/water wash to remove some oxygenates), which was filed on August 6, 2003, the entireties of which are incorporated herein by reference. One exemplary non-limiting separation system is illustrated in Figure 1.

[0040] As shown, compressed product stream 128 is directed to a C3-separation zone 129. Compressed product stream 128 may include methanol, ethanol, DME, ethanal, propanal, acetone, isopropyl alcohol or a mixture thereof, in addition to ethane, ethylene and propylene. The C3-separation zone 129 separates ethylene and propylene, as well as lighter components, from at least some of the DME and heavier components, including C4 olefins, C5+ hydrocarbons, unreacted methanol, and methanol remaining from the optional water absorption unit. The C3-separation zone 129 includes one or more separation units, e.g., distillation columns, which are adapted to separate C3-components from some of the DME and heavier components. Additional methanol, not shown, optionally is added to the C3-separation zone 129 to reduce hydrate and/or free water formation. A majority of the ethylene and propylene from compressed product stream 128 exits the C3-separation zone 129 via C3-overhead stream 130. Some of the DME and heavier components, which include C4+ olefins and C5+ hydrocarbons, exits the C3-separation zone 129 through C4+ bottoms stream 141.

[0041] The C3-components in C3-overhead stream 130 preferably are directed to a caustic wash unit 131, in which the C3-overhead stream 130 contacts a caustic wash medium under conditions effective to remove carbon dioxide and carbonic acid therefrom and form CO₂ depleted stream 132. Preferably, the caustic wash medium is sent through a line, not shown, to the top portion of the caustic wash unit 131 to remove carbon dioxide, which is entrained in the C3-overhead stream 130. Spent caustic leaves the caustic wash unit 131 through a waste caustic line, not shown.

[0042] Caustic treated ethylene and propylene exits caustic wash unit 131 through CO₂ depleted stream 132 and preferably is directed to a water wash column, not shown, and/or to drying section 133. Water enters the optional water wash column and water and absorbed components exit the water wash column through a bottoms line, not shown. Water washed ethylene and propylene exit the

water wash column through an overhead line, not shown, and pass through a drying section 133. Dry product stream 134 optionally contains less than 5 weight percent water, less than 1 weight percent water, or less than 0.5 weight percent water, based on the total weight of the dry methanol stream 134. Dry product stream 134 exits the drying section 133 and is directed to a C2/C3 separation system 135.

[0043] In one embodiment of this invention, separation is by conventional distillation. Distillation is carried out using a vessel or tower having internal packing or trays that creates a temperature difference from top to bottom of the tower. The upper portion of the tower is the cooler portion, and higher volatile components in the feed exit from the top of the tower. C2/C3 separation system 135 preferably includes one or more cryogenic fractionation columns. The C2/C3 separation system 135 preferably forms a tail gas stream 136, an ethylene product stream 137, and a propylene product stream 138. Optionally, the tail gas stream 136 is first removed from the C2+ components in dry product stream 134, and C2 components are then separated from C3 components. Alternatively, the C3 components are removed from the C2- components (including the light ends, which form the tail gas) in a first separation step followed by tail gas separation from the C2 components in a second step.

[0044] The tail gas stream 136 preferably includes the majority of the methane and hydrogen that was present in the dry product stream 134; the ethylene product stream 137 preferably includes a majority of the ethylene that was present in the dry product stream 134; and the propylene product stream 138 preferably includes a majority of the propylene that was present in the dry product stream. The ethylene product stream 137 preferably is used as a monomer for the formation of polyethylene. The tail gas stream 136 optionally is burned as a fuel in one or more of the steps of the OTO reaction process.

[0045] According to the present invention, the C2/C3 separation system 135 is designed so that propylene product stream 138 contains one or more oxygenate contaminants. At least a portion of the propylene product stream 138 preferably is directed to one or more derivative non-polymerization reactor units for conversion of the propylene to one or more derivative non-polymer products.

[0046] The oxygenate contaminant optionally is selected from one or more of methanol, ethanol, dimethyl ether (DME), ethanal, propylene, acetone, isopropyl alcohol or a mixture thereof. The propylene product stream 138 optionally comprises at least about 1 wppm, at least about 5 wppm, at least about 10 wppm, at least about 1000 wppm, at least about 1 weight percent, at least about 2 weight percent, or at least about 5 weight percent oxygenate contaminants, based on the total weight of the propylene product stream. Preferably, the propylene product stream 138 comprises less than 10 weight percent oxygenate contaminants, based on the total weight of the propylene product stream 138.

[0047] Figure 2 illustrates a preferred separation system, which may be implemented according to the present invention, and which provides a propylene-containing stream that may be suitable for disposition to one or more non-polymerization derivative reaction processes according to the present invention. As shown, an effluent stream 200 is provided, which contains ethane, ethylene, propane, propylene and a minor amount of one or more oxygenates such as methanol, ethanol, dimethyl ether (DME), ethanal, propanal, acetone, isopropyl alcohol and/or a mixture thereof. Preferably, the effluent stream 200 is derived from an OTO reaction system, not shown, and optionally has been quenched to remove a substantial amount of water therefrom.

[0048] The effluent stream 200 is directed to first separation unit 201, which preferably is a wash column adapted to remove some of the non-DME oxygenates from the initial effluent stream 200. A majority of the C4+ hydrocarbon components preferably are removed, e.g., through distillation, from the effluent stream 200 prior to its introduction into first separation unit 201. In the first separation unit 201, the effluent stream 200 contacts an oxygenate removal medium 202, preferably methanol, under conditions effective to remove some of the oxygenates therefrom. This means that ethane, ethylene, propane, propylene and at least some oxygenates are recoverable in a first overhead stream 203, with the bulk of the oxygenate removal medium 202, and some oxygenates being recoverable in a first bottoms stream 204. The first overhead stream 203 also likely contains a minor amount of residual oxygenate removal medium. The first separation unit 201 optionally includes a reflux line and/or a reboiler line and

corresponding heat exchangers, not shown, to facilitate separation of these components.

[0049] First overhead stream 203 is then directed to a second separation unit 210, which preferably is a water wash column adapted to separate any residual oxygenate removal medium 202 carried over from the first separation unit 201 via first overhead stream 203. Specifically, in second separation unit 210, the first overhead stream 203 contacts water 209 under conditions effective to remove at least a majority of the residual oxygenate removal medium therefrom. Thus, ethane, ethylene, propane, propylene and oxygenates from the first overhead stream 203 are recoverable in a second overhead stream 211, with the bulk of the residual oxygenate removal medium 202 and water 209 being recoverable in a second bottoms stream 218. The second separation unit 210 optionally includes a reflux line and/or a reboiler line and corresponding heat exchangers, not shown, to facilitate separation of these components.

[0050] Optionally, second overhead stream 211 is directed to a caustic wash unit, not shown, to remove carbon dioxide, and/or a drying unit, not shown. Reverting to Fig. 2, second overhead stream 211 preferably is directed to demethanizer feed train 212. Demethanizer feed train 212 is a “cold box” that preferably is formed of a series of coolers, e.g., core exchangers, and knock out drums, not shown, that cool second overhead stream 211 and form a plurality of cooled streams 214A-C. Cooled streams 214A-C may be in liquid and/or vapor form. Preferably, cooled streams 214A-C are directed to a third separation unit 215 for further processing. The third separation unit 215 preferably is a distillation column adapted to separate light ends such as methane, hydrogen and/or carbon monoxide from ethane, ethylene, propane, DME and propylene. Specifically, the third separation unit 215 separates the cooled streams 214A-C, collectively, into a third overhead stream 216, which contains a majority of the light ends that were present in the cooled streams 214A-C, and a third bottoms stream 217, which preferably contains a majority of the ethane, ethylene, propane, oxygenates and propylene that was present in the cooled streams 214A-C. The third separation unit 215 optionally includes a reflux line and/or a reboiler line and corresponding heat exchangers, not shown, to facilitate separation of the light

ends from ethane, ethylene, propane, oxygenates and propylene. Third overhead stream 216 optionally is used as a cooling medium for cold box 212, and exits therefrom via tail gas stream 213.

[0051] Third bottoms stream 217 preferably is introduced into a fourth separation unit 206. The fourth separation unit 206 preferably is a distillation column adapted to separate C2- components from C3+ components. Specifically, the fourth separation unit 206 separates the third bottoms stream 217 into a fourth overhead stream 207, which contains a majority of the ethane and ethylene that was present in the third bottoms stream 217, and a fourth bottoms stream 208, which preferably contains a majority of the propane, oxygenates and propylene that was present in the third bottoms stream 217. The fourth separation unit 206 optionally includes a reflux line and/or a reboiler line and corresponding heat exchangers, not shown, to facilitate separation of the C2- components from the C3+ components. The fourth overhead stream 207, optionally is directed to C2 splitter, not shown, for separation of ethane from ethylene.

[0052] If the effluent stream 200 was depleted in C4+ components, then the fourth bottoms stream 208 may, depending on the amount of propane and oxygenate contaminants in the effluent stream 300, contain mostly propylene and a minor amount of oxygenate contaminants, and may be well-suited for one or more derivative non-polymerization reaction processes according to the present invention. If higher quality propylene is desired, then the fourth bottoms stream 208 optionally is introduced into fifth separation unit, not shown, for removal of additional propane and/or oxygenate components. The fifth separation unit preferably is a distillation column, e.g., a propane purge tower, adapted to separate propylene from propane and some oxygenates.

[0053] If the effluent stream 200 contains C4+ components in any appreciable quantity, then the process flow scheme according to the present invention preferably includes a depropanizer, not shown. The depropanizer is adapted to separate C4+ components from C3- components, e.g., light ends, ethylene, ethane, propylene, propane and DME. The placement of the depropanizer may vary widely. In the embodiment illustrated in Fig. 2, the depropanizer optionally receives and removes at least a majority of the C4+

components from one or more of the following streams: the effluent stream 200, the second overhead stream 211, the third bottoms stream 217 or the fourth bottoms stream 208.

[0054] If the effluent stream 200 contains acetylene, methyl acetylene, propadiene, or other multiply unsaturated components, then the system of the present invention preferably includes a hydrogenation converter, e.g., an acetylene or MAPD converter, not shown. If incorporated into the present invention, the hydrogenation converter preferably receives and processes one or more of the following streams: the second overhead stream 211, the third bottoms stream 217, the fourth overhead stream 207 and/or the fourth bottoms stream 208. In the hydrogenation converter, acetylene contacts hydrogen and carbon dioxide under conditions effective to convert at least a portion of the acetylene to ethylene. Similarly, methyl acetylene and/or propadiene contact hydrogen and carbon dioxide under conditions effective to convert at least a portion of the methyl acetylene and/or propadiene to propylene. Components other than acetylene, methyl acetylene and propadiene that are present in the above-identified streams preferably pass unaltered through the hydrogenation converter(s). The resulting acetylene-depleted streams are then processed as described above with reference to Fig. 2.

[0055] Several non-polymerization derivative reaction processes according to the present invention will now be disclosed in greater detail.

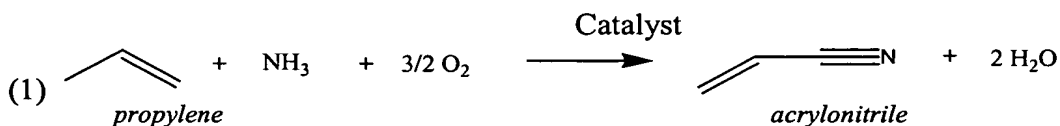
Ammonoxidation of Propylene to Form Acrylonitrile

[0056] Acrylonitrile is the most-produced non-polymerization propylene derivative product. In the year 2000, 5.4 million tons of the world's propylene, or about 10 percent, was used to synthesize acrylonitrile. Acrylonitrile is used virtually exclusively as an intermediate. Specifically, most of the acrylonitrile produced is used for acrylic fibers, ABS (acrylonitrile-butadiene-styrene) or SAN (styrene-acrylonitrile) copolymers for engineering plastic applications, adiponitrile (an intermediate for Nylon-66) or other nitrile-based elastomers. The largest use of acrylonitrile is in the manufacture of adiponitrile.

[0057] Acrylonitrile also polymerizes to form polyacrylonitrile or ORLON. The initiator for the polymerization typically is a mixture of ferrous

sulfate and hydrogen peroxide. These two compounds react to produce hydroxyl radicals ($\cdot\text{OH}$), which act as chain initiators. Polyacrylonitrile may be dissolved in N,N-dimethylformamide to form a solution that can be used to spin fibers. Fibers produced in this process are used in making carpets and clothing.

[0058] Nearly all of the world's supply of acrylonitrile is produced by vapor phase ammoxidation of propylene. While not limiting the invention to a specific derivative non-polymerization chemical reaction or reaction mechanism, the ammoxidation of propylene may be illustrated as follows:



[0059] The original well-known catalyst systems were based upon a bismuth phosphomolybdate (Bi, Mo, P) catalyst system as described in U.S. Patent No. 2,904,580, the entirety of which is incorporated herein by reference. U.S. Patents Numbers 3,230,246 and 3,658,877, the entireties of which are incorporated herein by reference, show that this mixed oxide catalyst system, while fairly highly selective toward the desired acrylonitrile product, also exhibits considerable yields of acrolein. Subsequent advances in catalyst technology were aimed at improving the acrylonitrile yields and propylene utilizations. Catalyst compositions employed in this service comprise antimony-uranium (Sb-U) combinations, iron, or bismuth, molybdenum, and phosphorus (Fe, Bi, Mo, P) combinations, and in some instances copper, selenium or tellurium (Cu, Se, Te) are added as promoters, as described, for example, in U.S. Patent Nos. 3,658,877; 4,156,660; 4,609,502; 4,618,593; 4,659,689; 4,424,141; 4,316,856; 4,317,747; and 4,322,368, the entireties of which are incorporated herein by reference. Preferably, the catalyst is an oxidic structure of the bismuth molybdate or bismuth ferromolybdate types, which are well-known in the art.

[0060] In one reaction process, chemical grade propylene, oxygen (as air), and ammonia are catalytically converted to acrylonitrile using a fluidized bed gas phase reactor. Typical operating temperatures are from about 400°C to about 500°C, more preferably from about 400°C to about 450°C, and pressures are from about 3 psig (20.7 kPag) and about 30 psig (206.9 kPag). The acrylonitrile-

containing reactor effluent preferably is cooled and scrubbed with water in a counter-current absorber. The resulting aqueous solution contains the acrylonitrile and byproducts. This aqueous solution is then purified in a series of subsequent separation units, e.g., fractionation columns, that produce both crude acetonitrile, and fiber grade acrylonitrile as the major product streams.

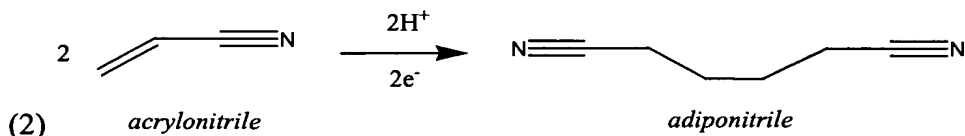
[0061] Typical byproducts from the propylene ammoxidation process include acetonitrile, hydrogen cyanide, and carbon oxides (CO and CO₂). However, the product quality specifications for acrylonitrile also commonly list acetone, acetic acid, acetaldehyde (typically all in the 10-500 wppm range) as possible contaminants. Thus, it has now been determined that the presence of one or more of these (or other) oxygenated hydrocarbon species in an OTO-derived propylene product stream is not significantly detrimental to the conversion of the propylene in the propylene product stream to acrylonitrile. That is, the acrylonitrile synthesis process is amenable to converting an OTO-derived propylene feedstock that may contain some level of these oxygenated contaminants to acrylonitrile. Accordingly, in one embodiment, the invention is directed to a process for forming acrylonitrile. The process includes providing a product stream containing propylene and an oxygenate contaminant. Preferably, the product stream is derived from an OTO reaction system, and more preferably from an MTO reaction system. The product stream is directed to an acrylonitrile derivative process reactor. In the acrylonitrile derivative process reactor, the propylene is converted to acrylonitrile. Preferably, the process includes contacting the propylene with ammonia, an oxygen-source, e.g., air, and a catalyst under conditions effective to form acrylonitrile. Preferably the catalyst is an oxidic structure of the bismuth molybdate or bismuth ferromolybdate types, which are well-known in the art.

[0062] Additional descriptions of acrylonitrile synthesis processes and catalysts used therein are described in *Kirk Othmer Encyclopedia of Chemical Technology*, 3rd edition, volume 1, pp. 414-426, and in *Ullman's Encyclopedia of Industrial Chemistry*, 5th edition, volume A1, pp. 177-184, the entireties of which are incorporated herein by reference, and in U.S. Patents Nos. 2,904,580; 3,658,877; 4,156,660; 4,609,502; 4,618,593; 4,659,689; 4,424,141; 4,316,856;

4,317,747; and 4,322,368, the entireties of which are incorporated herein by reference.

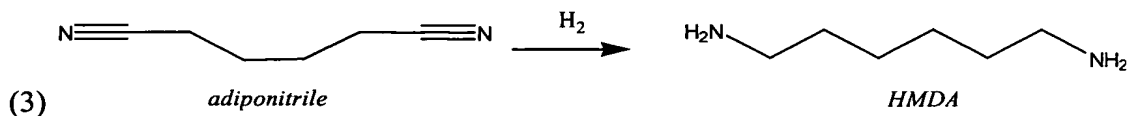
Synthesis of Adiponitrile from Acrylonitrile

[0063] As indicated above, the largest use of acrylonitrile is in the manufacture of adiponitrile. About one-third of the adiponitrile is formed by the electrohydrodimerization of acrylonitrile (the bulk of the remainder of adiponitrile is formed from the hydrocyanation of butadiene). Without limiting the invention to a particular mechanism, this reaction may be illustrated as follows:



[0064] Adiponitrile manufacture preferably is a head-to-head dimerization of acrylonitrile. The reaction occurs in a two-phase system using a phase transfer catalyst, well-known in the art. First, acrylonitrile is reduced to form a radical anion. Two radical anions couple simultaneously with protonation to form a C6 chain. Hydrogen transfer forms the final nitrile product. Thus, in one embodiment, the invention is directed to converting acrylonitrile, which is produced from a propylene-containing stream from an OTO reaction system, to adiponitrile.

[0065] Optionally, the adiponitrile formed from the OTO-derived propylene stream is hydrogenated to form hexamethylenediamine (HMDA), as is well-known to those skilled in the art. This reaction is illustrated as follows:



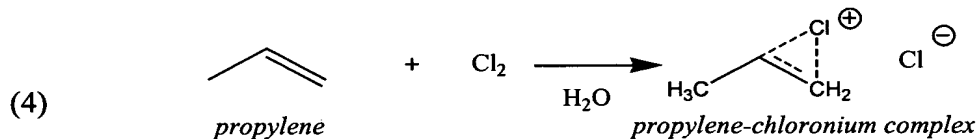
[0066] In one embodiment, the present invention is directed to a process for forming a adiponitrile and/or HMDA. The process includes providing a product stream containing propylene and an oxygenate contaminant. Preferably, the product stream is derived from an OTO reaction system, and more preferably from an MTO reaction system. The product stream is directed to an acrylonitrile derivative process reactor. In the acrylonitrile derivative process reactor, the

propylene is converted to acrylonitrile. Preferably, the process includes contacting the propylene with ammonia, an oxygen-source, e.g., air, and a catalyst under conditions effective to form acrylonitrile. Preferably the catalyst is an oxidic structure of the bismuth molybdate or bismuth ferromolybdate types, as is well-known in the art. The acrylonitrile is then optionally isolated and directed to an adiponitrile reactor, which optionally is the acrylonitrile derivative process reactor. In the adiponitrile reactor, the acrylonitrile contacts hydrogen and electrons from an electron source under conditions effective to convert at least a portion of the acrylonitrile to adiponitrile. Optionally, the adiponitrile is hydrogenated to form HMDA. This hydrogenation process may occur in the acrylonitrile derivative process reactor, the adiponitrile reactor or in a third reaction vessel, e.g., an HMDA synthesis unit.

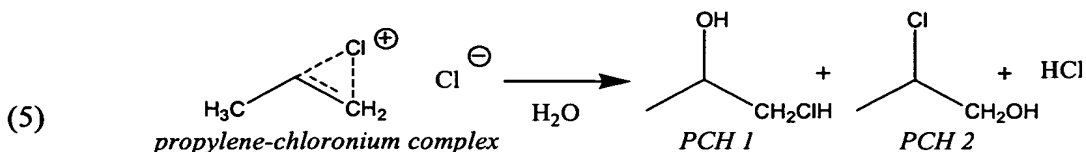
Direct and Indirect Oxidation of Propylene to Form Propylene Oxide

[0067] Like acrylonitrile, propylene oxide also is used primarily as an intermediate. The major dispositions for propylene oxide are to urethane polyether polyols for foam applications, to propylene glycol and to polypropylene glycol. In the year 2000, 3.8 million tons of the world's propylene, or about 7 percent, was used to synthesize propylene oxide.

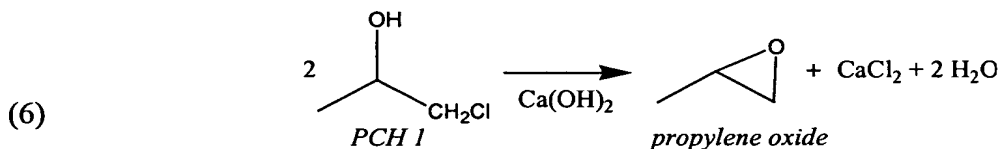
[0068] Conventional conversion of propylene to propylene oxide production is based upon the chlorohydrin process. In the first step of this process, gaseous propylene and chlorine are reacted in an aqueous solution to form a propylene-chloronium intermediate complex. Without limiting the present invention to a particular reaction or reaction mechanism, this step can be illustrated as follows:



[0069] The propylene-chloronium complex then reacts with water to form hydrochloric acid, and the propylene chlorohydrin isomers (PCH 1 & PCH 2):

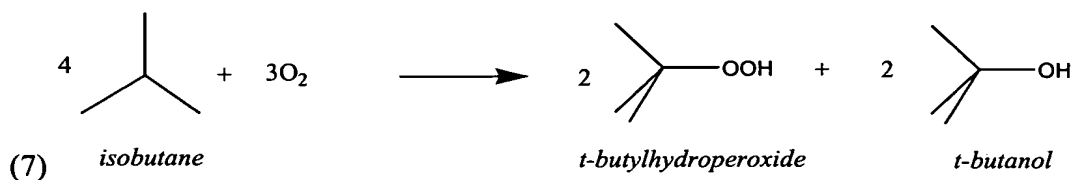


[0070] In the final epoxidation step, the aqueous chlorohydrin stream is reacted with a base (typically either calcium hydroxide, or sodium hydroxide caustic), to form the propylene oxide product:

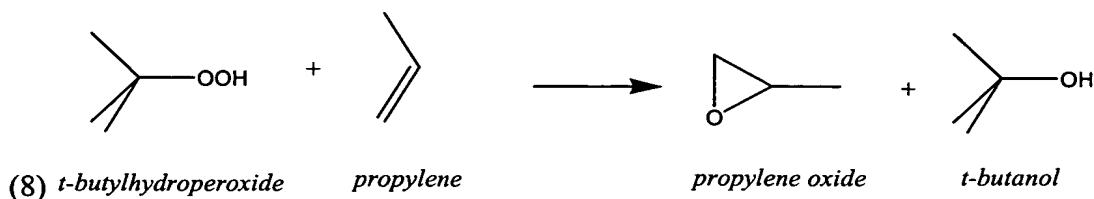


[0071] There are other variations of the chlorohydrin process that employ alternate sources of chlorine, or electrochemical methods for producing propylene oxide. Such processes are essentially the same chemistry but utilize the cell liquor from brine electrolysis cells.

[0072] Propylene oxide also may be formed through indirect oxidation of propylene. These indirect oxidation processes involve the use of hydrogen peroxide as the oxygen source. However, the high cost of hydrogen peroxide and the potential safety hazards associated with high concentrations of the peroxide are key disadvantages of these processes. The oxidation of propylene with organic hydroperoxides in the presence of catalysts now accounts for approximately half of the world's production of propylene oxide. One of the most common examples of this approach begins with isobutane oxidation to form equimolar amounts of t-butyl hydroperoxide and t-butanol.

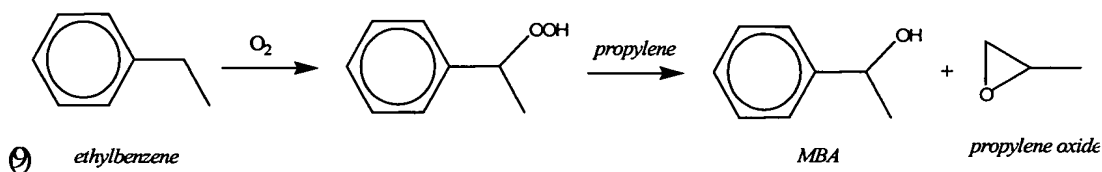


The t-butylhydroperoxide then reacts with the propylene to produce the propylene oxide and additional t-butanol, as follows:

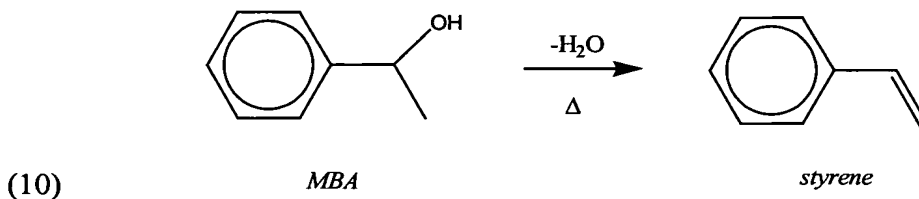


The presence of large concentrations of alcohols in the aqueous reaction mixture makes the indirect oxidation approach especially amenable to OTO-derived propylene streams that may contain concentrations of residual oxygenated byproducts.

[0073] Alternatively, ethylbenzene rather than isobutane is used for the initial hydroperoxide formation. Propylene then is reacted with the ethylbenzene hydroperoxide to form methyl benzyl alcohol (MBA) and propylene oxide, as follows:



The MBA product optionally is dehydrated at high temperatures to form styrene, as follows:



Styrene then can be polymerized through well-known techniques to form polystyrene.

[0074] Historically, molybdenum salts have been used as the epoxidation catalysts for the indirect oxidation of propylene to form propylene oxide. Thus, in one embodiment of the present invention, the catalyst implemented in the derivative reactor is a molybdenum complex in aqueous solution. More recently, however, titanium silicates or titanium containing zeolites have been used for this

purpose. A variety of different additives (for example cesium phosphate) can also be added to the aqueous solution to stabilize the pH of the reaction medium.

[0075] The first step of the indirect oxidation process involves formation of the hydroperoxide. As shown above, the isobutane (for example) is reacted with oxygen to form the hydroperoxide. This reaction occurs at temperatures between 120-140°C, and pressures from about 25 bar to about 35 bar. The crude peroxide stream is then passed to a series of epoxidation reactors, where it is allowed to contact a titanium silicate catalyst. Conditions in the epoxidation reactors get progressively more severe as the catalyst ages in order to maximize conversion of the hydroperoxide. Common reaction conditions are 110°C and 40 bar in the first reactor, and 120°C in the subsequent reactor. Optionally, the pressure in the subsequent reactor is slightly lower than the pressure in the first reactor to allow the transfer of the contents between the reactors. The hydroperoxide selectivity to propylene oxide is about 80 weight percent, reflecting decomposition of the peroxide to other species (the crude peroxide stream contains small amounts of aldehyde and ketone byproducts).

[0076] The epoxidation reactor effluent is then subjected to a number of purification steps. Unreacted propylene preferably is recovered and recycled in a first purification step. Subsequently, the propylene oxide product is recovered. The coproduct t-butanol preferably is recovered in a final purification step.

[0077] Additional descriptions of propylene oxide synthesis processes, catalysts implemented therein and product separation techniques are described in *Ullman's Encyclopedia of Industrial Chemistry*, 5th edition, vol. A22, pp. 239-260, the entirety of which is incorporated herein by reference, in U.S. Patents Nos. 3,458,534; 3,449,219; 3,360,584; and 3,592,857, the entireties of which are incorporated herein by reference, and in United Kingdom Patents Nos. 1,261,617 and 1,339,296, which are also incorporated herein by reference.

[0078] It has now been determined that the presence of one or more oxygenated hydrocarbon species in an OTO-derived propylene product stream is not significantly detrimental to the conversion of the propylene in the propylene product stream to propylene oxide, through either direct or indirect oxidation. That is, the propylene oxide synthesis processes are amenable to converting an

OTO-derived propylene feedstock that may contain some level of oxygenated contaminants to one or more of propylene oxide, propylene chlorohydrin, t-butanol, and/or MBA.

[0079] Accordingly, in one embodiment, the invention is directed to a process for forming one or more of propylene oxide, propylene chlorohydrin, t-butanol, and/or MBA. The process includes providing a product stream containing propylene and an oxygenate contaminant. Preferably, the product stream is derived from an OTO reaction system, and more preferably from an MTO reaction system. The product stream is directed to a propylene oxide derivative process reactor. In the propylene oxide derivative process reactor, the propylene is converted to one or more of propylene oxide, propylene chlorohydrin, t-butanol, and/or MBA. Optionally, the MBA is converted to styrene, and the styrene to polystyrene.

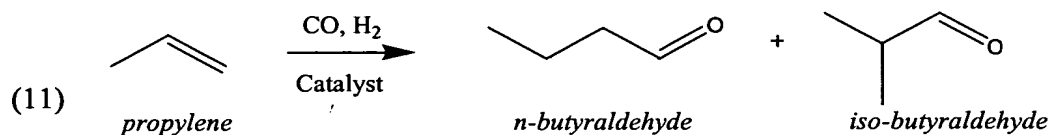
Propylene Hydroformylation to Form Butanals

[0080] In hydroformylation chemistry (sometimes referred to as Oxo chemistry), olefins are reacted with synthesis gas containing carbon monoxide and molecular hydrogen to form aldehydes products having one additional carbon atom. These aldehyde products have utility as intermediates in the manufacture of numerous commercially important chemicals. Thus, the invention further provides processes in which hydroformylation is followed by reactions to produce such chemicals. For example, the aldehyde products formed through the oxo reaction optionally are dimerized through Aldol reaction processes to form larger aldehydes, as discussed in more detail below. The Aldol products optionally are then hydrogenated to form one or more oxo alcohol products. Alternatively, the aldehyde products formed through the oxo reaction are hydrogenated to oxo alcohols without first undergoing an Aldol reaction.

[0081] The aldehyde products of this invention will have especial value when the aldehydes are aldolized, hydrogenated to saturated oxo alcohols, and the alcohols esterified, etherified or formed into acetals to give plasticizers or synthetic lubricants. In the year 2000, 3.8 million tons of the world's propylene, or about 7 percent, was used to synthesize oxo alcohols. Under circumstances where the olefin feed is ultimately derived from a low-value feedstock like natural

gas, e.g., in cases where methane from natural gas is converted to methanol and the methanol to olefin, the products or product mixtures from aldolization and hydrogenation may have value as liquid transportable fuels, optionally after dehydration to the olefin, and if desired hydrogenation to a paraffin or paraffinic mixture.

[0082] Without limiting the present invention to a particular reaction or reaction mechanism, the hydroformylation of propylene can be illustrated as follows:



[0083] The hydroformylation reaction can be carried out using conventional hydroformylation catalysts or catalyst precursors. The hydroformylation reaction involves contacting propylene, carbon monoxide and hydrogen in the presence of a hydroformylation catalyst or precursor. Hydrido transition metal carbonyls having the general formula $\text{HM}(\text{CO})_4$, where M is Co, Rh, or Ru, are typical catalysts for this reaction. Rhodium hydroformylation catalysts are particularly desirable in this invention because they are particularly tolerant to the presence of oxygenate contaminants that may be present in an OTO-derived propylene-containing stream. Suitable rhodium catalysts or catalyst precursors that can be implemented in this invention include rhodium(II) and rhodium(III) salts such as rhodium(III) chloride, rhodium(III) nitrate, rhodium(III) sulfate, potassium rhodium sulfate (rhodium alum), rhodium(II) or rhodium(III) carboxylate, preferably rhodium(II) and rhodium(III) acetate, rhodium(III) oxide, salts of rhodic(III) acid, triammonium hexachlororhodate (III).

[0084] Depending upon the catalyst used, the ratio of normal butyraldehyde to isobutyraldehyde produced can be controlled. The choice depends upon the ultimate end use for the aldehydes. Several significant advances in the hydroformylation catalyst systems include incorporating phosphorous-containing ligands, e.g., triphenylphosphine or phosphite, for improved performance.

[0085] In one embodiment of the invention, hydroformylation is carried out using an oil-soluble rhodium complex comprising a low valence rhodium (Rh) complexed both with carbon monoxide and a triorganophosphorus compound. The triorganophosphorus compound can include one or more oil-soluble triarylphosphines, trialkylphosphines, alkyl-diaryl-phosphines, aryl-dialkylphosphines, triorganophosphites, particularly trialkylphosphites and triarylphosphites (in which list alkyl includes cycloalkyl), containing one or more phosphorus atoms per molecule capable of complexing with Rh by virtue of having a lone pair of electrons on the phosphorus.

[0086] In another embodiment, triorganophosphorus ligands can be used, which preferably have (a) a molar P:Rh ratio of at least about 2:1, (b) a total concentration of phosphorus of at least about 0.01 mol/l; and (c) a [P]/Pco ratio maintained in the reactor of at least about 0.1 mmol/l/kPa, where [P] is the total concentration of the phosphorus in solution, and Pco is the partial pressure of carbon monoxide in the gas phase.

[0087] Examples of triorganophosphorus ligands include trioctylphosphine, tricyclohexylphosphine, octyldiphenylphosphine, cyclohexyldiphenylphosphine, phenyldioctylphosphine, phenyldicyclohexylphosphine, triphenylphosphine, tri-p-tolylphosphine, trinaphthylphosphine, phenyl-dinaphthylphosphine, diphenylnaphthylphosphine, tri-(p-methoxyphenyl)phosphine, tri-(p-cyanophenyl)phosphine, tri-(p-nitrophenyl)phosphine, and p-N,N-dimethylaminophenyl(diphenyl)phosphine, trioctylphosphite or tri-p-tolylphosphite. An example of a bidentate compound which can be used is diphos-bis(diphenylphosphino)ethane.

[0088] Preferably, Rh concentration in the reaction mixture is in a range of from about 1×10^{-5} to about 1×10^{-2} moles/liter or, in effect, in a range of from about 1 to about 1000 ppm, preferably about 20 to about 500 ppm, based on the total weight of the solution.

[0089] Oxo chemistry is typically homogeneously catalyzed. Syngas and propylene are fed to the hydroformylation reactor where the aldehyde is formed. The higher olefin catalyst is desirably contacted with the olefin feed stream in solution. The solution can comprise an oily solvent or a mixture of such solvents.

For example, aliphatic and aromatic hydrocarbons (e.g., heptanes, cyclohexane, toluene), esters (e.g., dioctyl phthalate), ethers, and polyethers (e.g., tetrahydrofuran, and tetraglyme), aldehydes (e.g., propanal, butanal) the condensation products of the oxo product aldehydes or the triorganophosphorus ligand itself (e.g., triphenylphosphine).

[0090] Alternatively, as described in U.S. Pat. Nos. 4,248,802, 4,808,756, 5,312,951 and 5,347,045, which are each incorporated herein by reference, the catalyst may contain a hydrophilic group. In such a case, an aqueous medium may be used.

[0091] Rhodium can be introduced into the reactor as a preformed catalyst, for example, a solution of hydridocarbonyl tris(triphenylphosphine) rhodium(I); or it can be formed in situ. If the catalyst is formed in situ, the Rh may be introduced as a precursor such as acetylacetonatodicarbonyl rhodium(I) $\{\text{Rh}(\text{CO})_2(\text{acac})\}$, rhodium oxide $\{\text{Rh}_2\text{O}_3\}$, rhodium carbonyls $\{\text{Rh}_4(\text{CO})_{12}$, $\text{Rh}_6(\text{CO})_{16}\}$, tris (acetylacetonato) rhodium(I), $\{\text{Rh}(\text{acac})_3\}$, or a triaryl phosphine-substituted rhodium carbonyl $\{\text{Rh}(\text{CO})_2(\text{PAr}_3)\}_2$, wherein Ar is an aryl group.

[0092] The hydroformylation reaction is run between about 40°C and about 200°C, more preferably between about 90°C and about 180°C, and more preferably between about 110°C and about 150°C. The reaction is also desirably carried out at a low pressure, e.g., a pressure of about 0.05 to about 50 MPa (absolute), preferably about 0.1 to about 30 MPa, and most preferably below about 5 MPa. It is particularly preferred that carbon monoxide partial pressure be not greater than about 50% of the total pressure. The proportions of carbon monoxide and hydrogen used in the hydroformylation or oxo reactor at the foregoing pressures are desirably maintained as follows: CO from about 1 to about 50 mol %, preferably about 1 to about 35 mol %; and H₂ from about 1 to about 98 mol %, preferably about 10 to about 90 mol %.

[0093] The hydroformylation reaction can be conducted in a batch mode or, preferably, on a continuous basis. In a continuous mode, a residence time of up to 4 hours can be used. If a plurality of reactors is employed, a residence time

as short as 1 minute can be employed. Otherwise a preferred residence time is in the range of from about 1/2 to about 2 hours.

[0094] Since the hydroformylation process of the invention advantageously takes place in the liquid phase and the reactants are gaseous compounds, a high contact surface area between the gas and liquid phases is desirable to avoid mass transfer limitations. A high contact surface area between the catalyst solution and the gas phase can be obtained in a variety of ways. For example, by stirring in a batch autoclave operation. In a continuous operation, the olefin feed stream can be contacted with catalyst solution in, for example, a continuous-flow stirred autoclave where the feed is introduced and dispersed at the bottom of the vessel, preferably through a perforated inlet. Good contact between the catalyst and the gas feed can also be ensured by dispersing a solution of the catalyst on a high surface area support. Such a technique is commonly referred to as supported liquid phase catalysis. The catalyst can also be provided as part of a permeable gel.

[0095] The hydroformylation reaction can be performed in a single reactor. Examples of suitable reactors can be found in U.S. Pat. Nos. 4,287,369 and 4,287,370 (Davy/UCC); U.S. Pat. No. 4,322,564 (Mitsubishi); U.S. Pat. No. 4,479,012 and EP-A-114,611 (both BASF); EP-A-103,810 and EP-A-144,745 (both Hoechst/Ruhrchemie). Two or more reactor vessels or reactor schemes configured in parallel can also be used. In addition, a plug flow reactor design, optionally with partial liquid product backmixing, can give an efficient use of reactor volume.

[0096] It is preferred that the hydroformylation reaction be carried out more than one reaction zone or vessel in series. Suitable reactor configurations are disclosed, for example, by Fowler et al in British Patent Specification No. 1,387,657, by Bunning et al. in U.S. Pat. No. 4,593,127, by Miyazawa et al in U.S. Pat. No. 5,105,018, and by Unruh et al. in U.S. Pat. No. 5,367,106, the entireties of which are incorporated herein by reference. Examples of individual hydroformylation reactors can of the standard types described by Denbigh and Turner in "Chemical Reactor Theory" ISBN 0 521 07971 3, by Perry et al in "Chemical Engineers' Handbook" ISBN 0-07-085547-1 or any more recent

editions, e.g., a continuous stirred tank or a plug flow reactor with adequate contact of the gas and the liquid flowing through the reactor. Advantageously these plug flow reactor designs or configurations include ways of partial backmixing of the reactor product liquid, as explained, for example, by Elliehausen et al in EP-A-3,985 and in DE 3,220,858.

[0097] Product selectivities range between 90-98 weight percent, with the balance comprising byproducts, or secondary reaction products of the aldehydes themselves. These typically include C₄ alcohols, C₄ esters, aldehyde dimers, trimers, and condensation products. The presence of large concentrations of the oxygenates in the aqueous reaction mixture makes the indirect oxidation approach especially amenable to OTO-derived propylene streams that may contain concentrations of residual oxygenated byproducts.

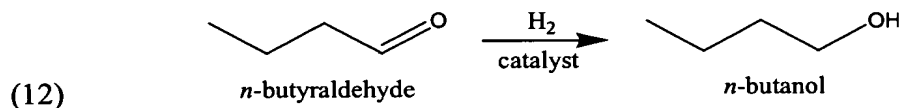
[0098] The reactor effluent preferably is flashed to separate the product aldehydes from the catalyst solution. Unreacted propylene and propane are recovered from the product stream via distillation or other separation technique and recycled. The crude aldehyde product is further fractionated to recover both the normal-, and branched aldehyde products.

[0099] More especially, the invention provides a process for the manufacture of butanol, wherein the butenal formed by hydroformylation is hydrogenated; a process for the manufacture of butyric acid, wherein the aldehyde product is oxidized; a process for the manufacture of an aldol dimer or trimer, wherein the aldehyde product is self-aldolized; a process for the manufacture of a saturated aldehyde, wherein the aldol dimer or trimer is hydrogenated to a corresponding saturated aldehyde; a process for the manufacture of an unsaturated alcohol, wherein the aldol dimer or trimer is selectively hydrogenated; a process for the manufacture of a saturated alcohol, wherein all double bonds in the aldol dimer or trimer are hydrogenated; a process for the manufacture of a saturated alcohol or acid, wherein the saturated aldehyde produced by hydrogenation of the aldol dimer or trimer is hydrogenated or oxidized to form the corresponding saturated alcohol or acid; a process for the manufacture of an ester, wherein the saturated alcohol or the acid is esterified; a process for the manufacture of an aldol tetramer or pentamer, or mixtures thereof, by aldolization of the aldehyde mixture

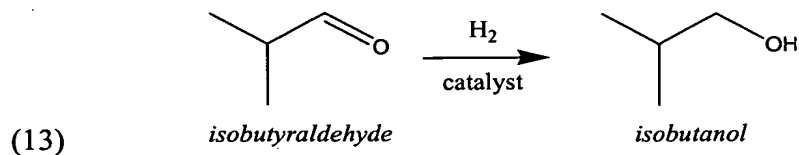
from hydroformylation; a process for the manufacture of a C₆ to C₂₀ alcohol or alcohol mixture, wherein the aldol dimer, trimer, tetramer, pentamer, or mixture, is hydrogenated to the corresponding alcohol or alcohol mixture; a process for the manufacture of liquid olefin or olefin mixture, wherein the tetramer or pentamer alcohol is dehydrated; and a process for the manufacture of a liquid paraffin or paraffin mixtures, wherein the olefin mixture is hydrogenated.

[0100] Additional descriptions of hydroformylation processes and the catalysts implemented therein are described in U.S. Patent Nos. 6,274,756; 6,030,930; 6,022,929; 5,675,041; 5,395,979; 5,382,701; 5,364,950; 5,298,669; 5,288,918; 5,288,818; 4,835,299; 4,687,874; 4,668,651; 4,642,388; 4,625,068; 4,599,206; 4,551,543; 4,528,404; 4,522,932; 4,473,505; 4,419,195; 4,404,119; 4,400,299; and 4,268,682, the entireties of which are incorporated herein by reference.

[0101] The hydroformylation product *n*-butyraldehyde is particularly valuable. The largest commercial use for *n*-butyraldehyde is in its reduction to form *n*-butanol, through the following reaction:



Similarly, isobutyraldehyde optionally is reduced to isobutanol, as follows:

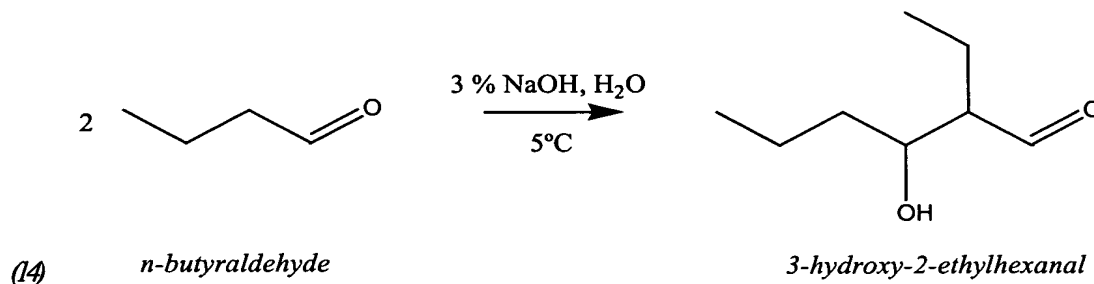


[0102] In these reactions, *n*-butyraldehyde and isobutyraldehyde are reduced to *n*-butanol and isobutanol, respectively, by hydrogen and a metal catalyst, by sodium in alcohol, and by lithium aluminum hydride. The reducing agent preferably is sodium borohydride (NaBH₄) or nickel on magesnia or copper chromite catalysts in fixed bed hydrogenation reactors with hydrogen at 140-200°C and 12-20 bar pressure.

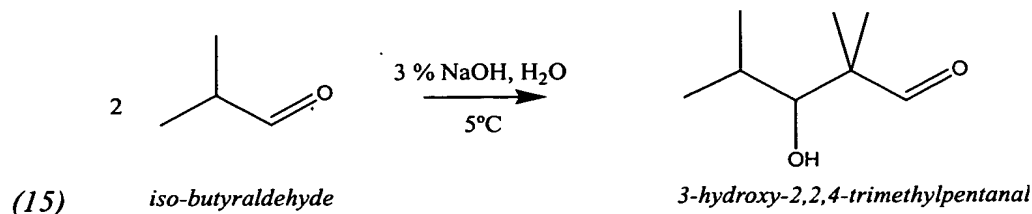
[0103] *n*-butanol can be subsequently converted through esterification to one or more of butyl acetate, butyl acrylate and butyl methacrylate. These esters have uses as solvents for coatings. Thus, the present invention is also directed to forming one or more of *n*-butanol, butyl acetate, butyl acrylate and butyl methacrylate from an OTO-derived propylene-containing feedstock.

[0104] If desired, the aldehydes formed in the hydroformylation process, described above, can undergo an Aldol addition to form longer chain unsaturated aldehydes (dimers). In this reaction, the aldehydes are subjected to basic conditions, preferably about 3 weight percent caustic solution (NaOH), in a countercurrent wash column at 120-150°C and 3-5 bar. Optionally, the aldehydes formed in the Aldol addition reaction process undergo an Aldol condensation reaction process, wherein the Aldol addition product is spontaneously converted to one or more partially unsaturated aldehydes.

[0105] Without limiting the present invention, one Aldol addition reaction can be illustrated as follows for the conversion of *n*-butyraldehyde to 3-hydroxy-2-ethylhexanal:



[0106] For the Aldol addition conversion of *iso*-butyraldehyde to 3-hydroxy-2,2,4-trimethylpentanal, the Aldol addition reaction can be illustrated as follows:



Optionally, the *n*-butyraldehyde reacts with iso-butyraldehyde in a similar Aldol addition and/or condensation reaction process.

[0107] Optionally, the Aldol addition or condensation product or products are subsequently reduced to one or more alcohols in a similar manner as shown above for *n*-butyraldehyde and isobutyraldehyde. For example, 3-hydroxy-2-ethylhexanal, above, optionally is hydrogenated in the presence of a catalyst, e.g., $\text{Co(PPh)}_3\text{KOH}$, and Octanoic acid to form 2-ethylhexanol. 3-hydroxy-2,2,4-trimethylpentanal optionally is hydrogenated to form 2,2,4-trimethylpentanol.

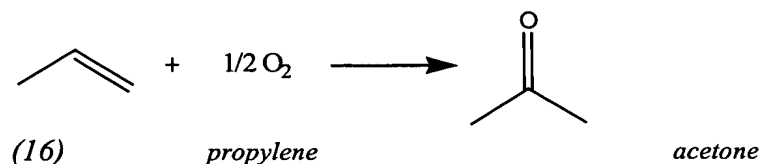
[0108] It has now been determined that the presence of one or more oxygenated species in an OTO-derived propylene product stream is not significantly detrimental to the conversion of the propylene in the propylene product stream to *n*-butyraldehyde and/or isobutyraldehyde through hydroformylation. That is, the *n*-butyraldehyde and isobutyraldehyde hydroformylation synthesis processes are amenable to converting an unpurified OTO-derived propylene feedstock that may contain some level of oxygenated contaminants to *n*-butyraldehyde and isobutyraldehyde.

[0109] Accordingly, in one embodiment, the invention is directed to a process for forming a *n*-butyraldehyde, and in another embodiment the invention is directed to a process for forming isobutyraldehyde. The processes include providing a product stream containing propylene and an oxygenate contaminant. Preferably, the product stream is derived from an OTO reaction system, and more preferably from an MTO reaction system. The product stream is directed to a derivative process reactor. In the derivative process reactor, the propylene is converted to *n*-butyraldehyde and/or isobutyraldehyde. Optionally, the invention includes directing the *n*-butyraldehyde to a second derivative non-polymerization reactor unit for converting the *n*-butyraldehyde to 3-hydroxy-2-ethylhexanal through an Aldol addition reaction process. Similarly, in another embodiment, the invention optionally includes directing the isobutyraldehyde to a second derivative non-polymerization reactor unit for converting the isobutyraldehyde to 3-hydroxy-2,2,4-trimethylpentanal through an aldol addition reaction process. The inventive process optionally includes converting a mixture of *n*-butyraldehyde and isobutyraldehyde, to 3-hydroxy-2-ethylhexanal and 3-hydroxy-2,2,4-

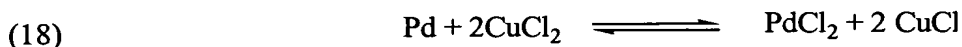
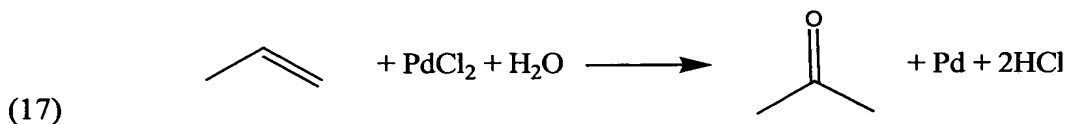
trimethylpentanal, respectively, in a single second derivative non-polymerization reactor unit. In one embodiment, the aldol addition or condensation product and/or the hydroformylation product (n-butyraldehyde and/or isobutyraldehyde) contacts hydrogen or a hydrogen-containing species in a hydrogenation unit under conditions effective to at least partially reduce the aldol addition/condensation product and or the hydroformylation product, e.g., to a corresponding alcohol or corresponding aliphatic species.

Propylene Oxidation to Form Acetone

[0110] In another derivative non-polymerization reaction process according to the present invention, propylene in a propylene-containing stream from an OTO reaction system is oxidized to form acetone. Acetone is commercially valuable in the production of acetone cyanohydrin, Bisphenol A, and as a solvent. Without limiting the present invention to a specific reaction or reaction mechanism, the overall reaction stoichiometry for direct propylene oxidation to acetone is given by:



[0111] However, the above reaction is actually the end result of the following elementary steps:



[0112] The catalyst for this process is an aqueous solution of a salt of a Group VIII metal (particularly palladium or rhodium) in combination with a copper or iron salt, which is used to complete the oxidation/reduction cycle and

preserve catalyst activity. As a result, propionaldehyde (propanal) is a major byproduct from this oxidation process. Other typical oxygenated hydrocarbon byproducts from this process include acetic acid, CO₂, propionic acid, and methyl acetate. Chlorinated hydrocarbons are also formed in small quantities as byproducts of this reaction. Also, since propylene is sparingly soluble in water, other oxygenated hydrocarbons such as acetic acid, ethylene glycol, or dioxane can be used to increase the miscibility of propylene in the catalyst solution.

[0113] Conceptually, the propylene oxidation process is similar to the ethylene oxidation to acetaldehyde process via the Wacker process. The Wacker process is an industrial process for the manufacture of ethanal by oxidizing ethylene. For example, bubbling ethylene and oxygen when treated by an acidified water solution of palladium and cupric chlorides yield acetaldehyde; reaction is catalyzed by PdCl₂ -CuCl₂. During the reaction palladium forms a complex with ethylene, is reduced to Pd(0), and is then reoxidized by Cu(II). The process is run in one vessel at 50-130°C and at pressures of 3-10 atm (303-1013 kPa). Regeneration of cupric chloride occurs in a separate oxidizer. The reactions are carried out in two alternating steps: First, an oxygen source such as air is used to oxidize the catalyst into the +2 oxidation state. In the second step, the oxygen source is replaced by propylene, the palladium oxidizes the propylene, and the palladium is re-oxidized by the excess of copper salt in the solution. Typical reaction temperatures are between about 110°C and about 120°C. Higher temperatures favor the formation of propionaldehyde and other side reaction byproducts of acetone. Typical reaction pressures are from about 5 atm (507 kPa) to about 12 atm (1216 kPa), with higher pressures increasing the solubility of propylene in the catalyst solution.

[0114] Additional descriptions of the oxidation of propylene to form acetone and of the catalysts implemented in this process are in Ullman's Encyclopedia of Industrial Chemistry, 5th edition, vol A1, pp. 79-96 and in U.S. Patent No. 3,149,167 (1964), the entireties of which are incorporated herein by reference.

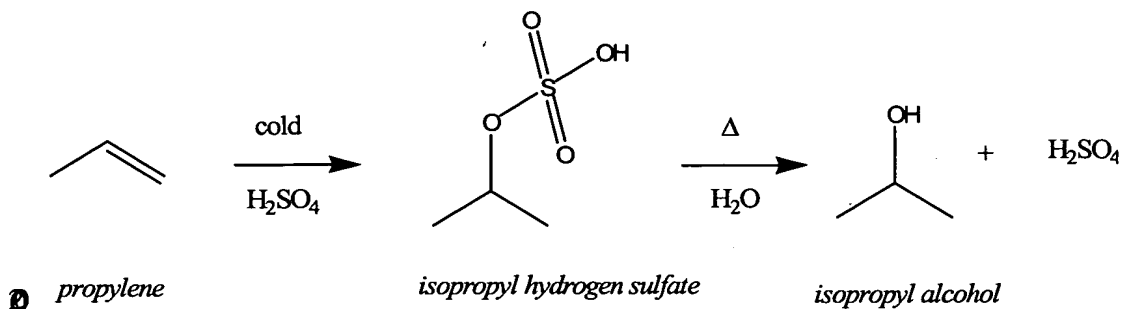
[0115] It has now been determined that the presence of one or more oxygenated hydrocarbon species in an OTO-derived propylene product stream is

not significantly detrimental to the conversion of the propylene in the propylene product stream to acetone. That is, the acetone synthesis process is amenable to converting an unpurified OTO-derived propylene feedstock that may contain some level of oxygenated contaminants to acetone. The process includes providing a product stream containing propylene and an oxygenate contaminant. Preferably, the product stream is derived from an OTO reaction system, and more preferably from an MTO reaction system. The product stream is directed to an acetone derivative process reactor. In the acetone derivative process reactor, the propylene is converted to acetone. Optionally a catalyst is implemented in the conversion of propylene to acetone. Preferably, the catalyst comprises $\text{PdCl}_2 \cdot \text{CuCl} \cdot \text{H}_2\text{O}$.

Hydration of Propylene to Form Isopropyl Alcohol

[0116] The major chemical process for the formation of isopropyl alcohol is the hydration of propylene. In another derivative non-polymerization reaction process according to the present invention, propylene in a propylene-containing stream from an OTO reaction system is hydrogenated to form isopropyl alcohol. Isopropyl alcohol is used as an industrial and household solvent, in coatings and as metallic catalysts in paints, inks and coatings. In the year 2000, 1.9 million tons of the world's propylene, or almost 4 percent, was used to synthesize isopropyl alcohol.

[0117] The synthesis of isopropyl alcohol is a well-known two-step process wherein propylene is first dissolved in cold concentrated sulfuric acid. Propylene is able to dissolve in concentrated sulfuric acid because the propylene reacts by addition to form an alkyl hydrogen sulfate. In the first step, propylene accepts a proton from sulfuric acid to form a carbocation, which reacts with a hydrogen sulfate ion to form an alkyl hydrogen sulfate. In the second step, the alkyl hydrogen sulfate is hydrolyzed to isopropyl alcohol by heating the alkyl hydrogen sulfate in water. The result of the addition of sulfuric acid to propylene followed by hydrolysis is a Markovnikov addition of -H and -OH. Without limiting the invention to a particular mechanism, the overall reaction can be illustrated as follows:



[0118] The highly acidic environment of the first step in the above synthesis process makes the synthesis of isopropyl alcohol highly amenable for implementing an unpurified propylene-containing stream from an OTO reaction system.

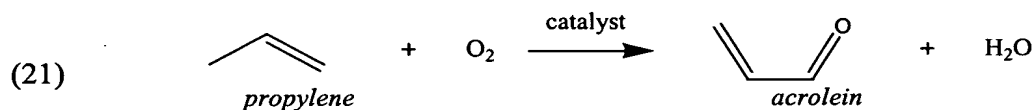
[0119] It has now been determined that the presence of one or more oxygenated hydrocarbon species in an OTO-derived propylene product stream is not significantly detrimental to the conversion of the propylene in the OTO-derived propylene product stream to isopropyl alcohol. That is, the isopropyl alcohol synthesis process, discussed above, is amenable to converting an unpurified OTO-derived propylene feedstock that may contain some level of oxygenated contaminants to isopropyl alcohol. The process includes providing a product stream containing propylene and an oxygenate contaminant. Preferably, the product stream is derived from an OTO reaction system, and more preferably from an MTO reaction system. The product stream is directed to an isopropyl alcohol derivative process reactor. In the isopropyl alcohol derivative process reactor, the propylene is converted to isopropyl alcohol. In one embodiment, the invention includes forming isopropyl hydrogen sulfate in a first reaction step, which optionally occurs in a first derivative reactor, and then hydrolyzing the isopropyl hydrogen sulfate to form the isopropyl alcohol product, optionally in the first derivative reactor or in a second derivative reactor. Optionally, the formation of isopropyl alcohol from propylene occurs in a single derivative reactor.

Oxidation of Propylene to Form Acrolein and Acrylic Acid

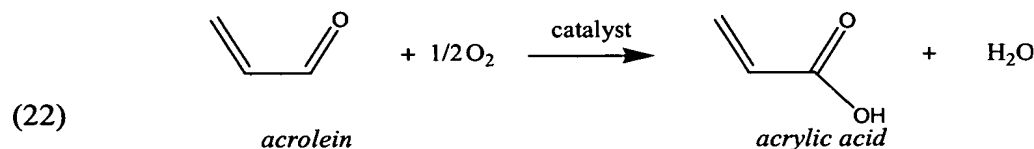
[0120] In another derivative non-polymerization reaction process according to the present invention, propylene in a propylene-containing stream

from an OTO reaction system is oxidized through catalytic vapor phase oxidation to form acrolein and/or acrylic acid. Acrolein is used almost exclusively as the key intermediate in forming acrylic acid. Acrylic acid may be converted into acrylate esters (such as methyl methacrylate) or is polymerized to polyacrylic acid or other copolymer products. In the year 2000, 1.9 million tons of the world's propylene, or about 3.5 percent, was used to synthesize acrylic acid.

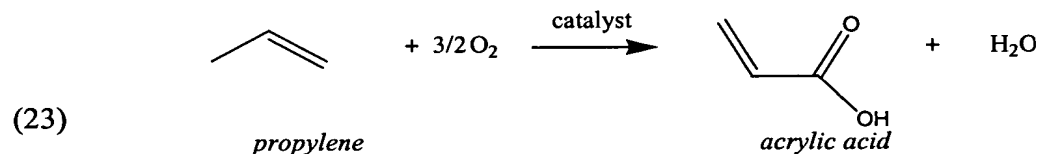
[0121] In one embodiment of the present invention, propylene is oxidized to acrolein (2-propenal). While not limiting the invention to a particular reaction or reaction mechanism, the oxidation of propylene to acrolein may be illustrated as follows:



[0122] The catalytic vapor phase oxidation of propylene to acrylic acid is carried out in two steps. The first step is the catalytic vapor phase oxidation of propylene to acrolein, shown above. The acrolein product is then further oxidized to form acrylic acid, as follows:



[0123] Catalyst systems have also been developed that promote the direct synthesis of acrylic acid from propylene:



[0124] The major side reactions that occur in these reaction processes produce CO and CO₂. Acetic acid, formaldehyde, and/or acetaldehyde in minor amounts are also produced through side reactions. However, there are pathways that yield smaller amounts of oxygenates such as acetic acid, formaldehyde, and/or acetaldehyde.

[0125] The first commercial catalysts for propylene oxidation were based upon copper oxide. These systems exhibited low propylene conversion activity, and low selectivity to acrolein. The subsequent use of bismuth molybdate catalyst compositions improved selectivity to acrolein, but still exhibited relatively low propylene conversion. Modern catalyst systems are still based upon this bismuth molybdate system, although numerous additional metals have been found to improve both activity and selectivity of the system. Common catalyst compositions for propylene oxidation comprise one or more of Mo, Bi, Fe, Ni, P, Co, K, W, Si, Cr, and Sn. In addition, catalyst systems comprising B, Na, Mg, Tl, and Sm, have also been demonstrated. See, for example, U.S. Patent Nos. 3,825,600 (1974); 3,454,630 (1969); 3,778,386 (1973); 3,833,649 (1972); 4,008,280 (1972); FR Pat. No. 2,028,164; JP Pat. Nos. 32,048 (1972); 41,329; and 34,111 (1973); BE Pat. No. 769,508 (1972); DE Pat. Nos. 2,165,335; 2,338,111 (1973); 3,125,062; and 3,125,061 (1981); and EP Pat. No. 663 (1977), the entireties of which are all incorporated herein by reference. Typical operating conditions for these modern catalyst systems are in the range of from about 300°C to about 355°C, and from about 150 kPa to about 250 kPa reactor pressure. Contact times vary between about 1.5 to about 3.5 seconds, and the propylene feed concentrations is in the range of 5-8 molar percent. Propylene conversions are typically between 90-99+ weight percent with these catalysts. Acrolein and acrylic acid selectivities are between 70-90 weight percent and 4-20 weight percent, respectively, with these systems.

[0126] Recent advances have shown alternative pathways to form acrolein from propylene via thermal oxidation or photo-oxidation of propylene over zeolite catalysts. See, for example, U.S. Patent Nos. 5,914,013; 5,827,406 and 6,329,553, the entireties of which are incorporated herein by reference.

[0127] The single-step process for acrylic acid formation employs catalyst systems comparable to those described above, except that the principle components are molybdenum oxide and tellurium oxide. The overall yield of the single-step process is relatively low (50-60% maximum). Thus, most acrylic acid processes are based upon the two-step approach. The first stage catalysts are selected from the acrolein-selective systems described above. Acrylic acid is

produced at high selectivity in the second stage using catalysts comprising oxides of molybdenum and vanadium, promoted with other metals such as Al, Cu, W, Mn, Fe, Sb, Cr, Sr, or Ce. See, for example, U.S. Patent Nos. 3,567,772; 3,644,509 and 3,845,120; JP Pat. Nos. 26,287; 11,371 and 169; BE Pat. No. 698,273; GB Pat. No. 1,267,189; DE Pat. Nos. 2,164,905; 2,413,206 and 2,152,037; FR Pat. No. 2,032,915; and DE-OS Pat. No. 2,055,155, the entireties of which are incorporated herein by reference.

[0128] The conversion and selectivity data for these catalyst systems clearly show that sum of the acrolein and acrylic acid selectivities are always lower than the overall propylene conversion. The difference between these values represents the selectivity of the catalyst to other byproducts, e.g., CO, CO₂, or various oxygenated hydrocarbons. Typically, this difference is in the range of 2-5%. Thus, these catalysts, and this process should be amenable to a propylene feedstock containing oxygenates.

[0129] In acrolein and acrylic acid syntheses, liquid propylene (typically chemical grade propylene containing 95 weight percent propylene and 5 weight percent propane) is vaporized, mixed with air, and compressed before being diluted with about 250 psia (1724 kPaa) steam. The olefin feed is preheated to about 400°F (204°C) before being introduced to a first oxidation reactor. Typical operating conditions in this reactor are 41 psia (283 kPaa). The reactor preferably is a shell and tube design, with molten salt on the shell side used as the cooling medium. The effluent gas from the first reactor is mixed with additional hot air and steam, heated to 460°F (238°C), and introduced to a second reactor for further oxidation and form a second reactor effluent. The second reactor effluent preferably is cooled, and directed to a quench absorber tower. Preferably, water is used in the quench column to absorb the acrylic acid product, as well as unreacted acrolein, and other non-volatile byproducts such as CO and CO₂. The bottoms stream preferably is passed to an azeotropic distillation column, wherein the acrylic acid is recovered from the other components in the bottoms stream. Typically, MIBK (methylisobutylketone) is used in this service because it azeotropes with the water.

[0130] Additional descriptions of the oxidation of propylene to form acrolein and/or acrylic acid and of the catalysts implemented in this process are described in *Ullman's Encyclopedia of Industrial Chemistry*, 5th edition, vol A1, pp. 149-176; *Kirk Othmer Encyclopedia of Chemical Technology*, 3rd edition, vol 1., pp. 277-297; and in *Kirk Othmer Encyclopedia of Chemical Technology*, 4th edition, vol 1, pp. 232-250, the entireties of which are incorporated herein by reference, as well as in U.S. Patents Nos. 3,825,600; 3,454,630; 3,778,386; 3,833,649; 4,008,280; 5,914,013; 5,827,406; 6,329,553; 3,567,772; 3,644,509; and 3,845,120, the entireties of which are also incorporated herein by reference. Further descriptions of these processes are also described in French Patents Nos. 2,028,164 and 2,032,915; German Patents Nos. 2,165,335; 3,125,061; 3,125,062; 2,338,111; DE-OS 2,055,155; 2,152,037; 2,413,206 and 2,164,905; Japan Patents Nos. 32,048; 41,329; 34,111; 26,287; and 11,371; Great Britain Patent No. 1,267,189; Belgium Patents Nos. 769,508 and 698,273; and EP Patent No. 663 (1977), the entireties of which are all incorporated herein by reference.

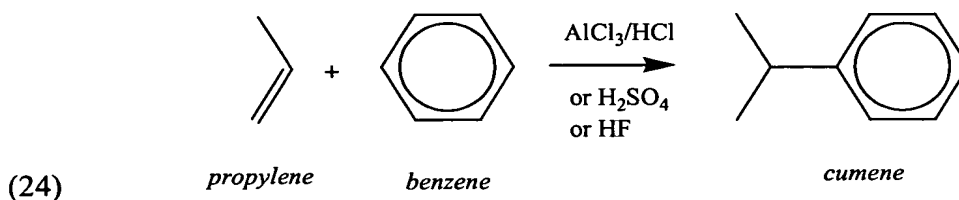
[0131] It has now been determined that the presence of one or more oxygenated hydrocarbon species in an OTO-derived propylene product stream is not significantly detrimental to the conversion of the propylene in the propylene product stream to acrolein and/or acrylic acid. That is, the acrolein and acrylic acid synthesis processes are amenable to converting an unpurified OTO-derived propylene feedstock that may contain some level of oxygenated contaminants to these products. The process includes providing a product stream containing propylene and an oxygenate contaminant. Preferably, the product stream is derived from an OTO reaction system, and more preferably from an MTO reaction system. The product stream is directed to a derivative process reactor. In the derivative process reactor, the propylene is converted to acrylic acid and/or acrolein. Optionally, the invention includes forming acrolein in a first reaction step, which may occur in a first derivative reactor, and then further oxidizing the acrolein to form the acrylic acid product, optionally in a second derivative reactor. Optionally, the formation of acrylic acid from propylene occurs in a single derivative reactor in a direct synthesis process, and optionally in a single conversion process. In one embodiment, a catalyst is implemented in the

conversion of propylene to acrolein and/or acrylic acid. Preferably, the catalyst comprises a complex oxide based upon molybdenum and bismuth in combination with one or more of cobalt, iron phosphorous or nickel, particularly in the acrolein synthesis reaction. In another embodiment, particularly desirable in the synthesis of acrylic acid, the catalyst is an oxide of a metal selected from the group consisting of molybdenum, vanadium optionally with one or more of tungsten, copper, iron or manganese.

Synthesis of Cumene from Propylene and Benzene

[0132] In another derivative non-polymerization reaction process according to the present invention, propylene in a propylene-containing stream from an OTO reaction system is reacted with an acid and benzene to form cumene (isopropylbenzene). Cumene is an important intermediate in the manufacture of phenol and acetone, discussed below. In the year 2000, 3.3 million tons of the world's propylene, or about 6 percent, was used to synthesize cumene.

[0133] Specifically, propylene reacts with benzene in the presence of an acid via a Friedel-Crafts alkylation mechanism to form the alkylbenzene cumene. Catalysts normally employed in new plants are zeolite-based, although older plants using aluminum chloride (AlCl_3) or phosphoric acid supported on kieselguhr as catalyst are still operating. The reaction begins with the addition of H^+ to propylene to form a carbocation. The carbocation then acts as an electrophile in a second step and attacks the benzene ring to form an arenium ion. The arenium ion then loses a proton to generate cumene. Without limiting the invention to a particular reaction mechanism, the overall stoichiometry for the reaction of propylene with benzene to form cumene may be illustrated as follows:



[0134] In one embodiment, propylene and benzene are brought into contact with a catalyst at high temperature and pressure in a fixed bed reactor.

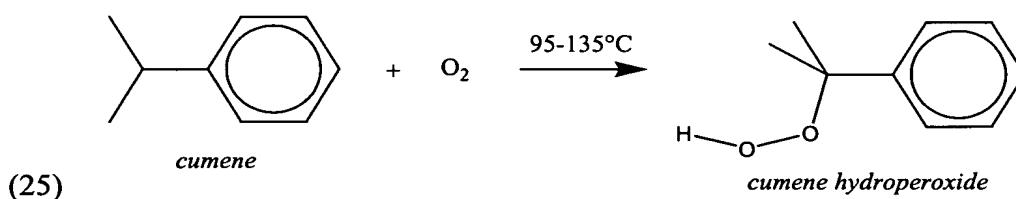
Various catalysts may be implemented in the alkylation of benzene to form cumene. The reaction is exothermic, and the reactor effluent optionally is utilized as a heating agent to heat incoming feed (propylene and/or benzene). The benzene preferably is provided in excess to suppress dealkylation and side reactions. Ideally, the ratio of benzene to propylene in the reaction mixture is about 10:1.

[0135] Typically, the cumene process uses chemical grade propylene (nominally 98% propylene), however, refinery grade propylene (nominally 70% propylene) can also be used. Oxygenate levels in chemical or refinery grade propylene can range from as little as 10 wppm to as high as several wt%. As the cumene synthesis process occurs under highly acidic conditions, it has now been determined that the presence of one or more of these (or other) oxygenated hydrocarbon species in an OTO-derived propylene product stream will not be significantly detrimental to the conversion of the propylene in the OTO-derived propylene product stream to cumene. That is, the cumene synthesis process is amenable to converting an OTO-derived propylene feedstock that may contain some level of these oxygenated contaminants to cumene. Accordingly, in one embodiment, the invention is directed to a process for forming cumene. The process includes providing a product stream containing propylene and an oxygenate contaminant. Preferably, the product stream is derived from an OTO reaction system, and more preferably from an MTO reaction system. The product stream is directed to a cumene derivative process reactor. In the cumene derivative process reactor, the propylene is reacted with benzene to form cumene. Preferably, the process includes contacting the propylene with benzene, over an acid catalyst, preferably a zeolite, AlCl_3 , or solid phosphoric acid supported on kieselguhr, under conditions effective to form cumene.

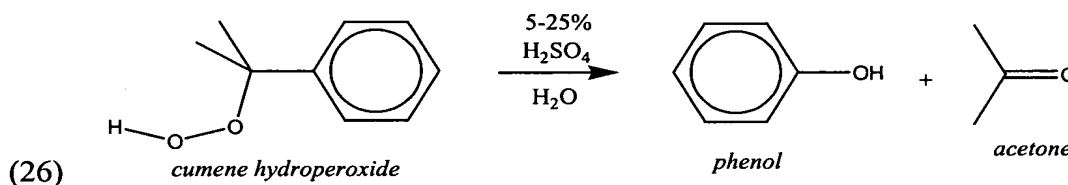
Reaction of Cumene with Oxygen to Form Acetone and Phenol

[0136] According to one embodiment of the present invention, cumene formed from a propylene-containing stream derived from an OTO reaction system is converted to phenol and acetone. Phenol is a very important article of commerce. Worldwide production is more than 3 million tons per year. Phenol is a starting material for the production of phenol-formaldehyde resins, which are

polymers that have a variety of uses, including plywood adhesives, glass fiber (Fiberglass) insulation, and molded phenolic plastics used in automobiles and appliances. Acetone is commercially valuable in the production of acetone cyanohydrin, Bisphenol A, methyl methacrylate, poly(methyl methacrylate) and as a solvent. The formation of phenol preferably occurs in a two step process. In the first step, cumene undergoes an autoxidation reaction with molecular oxygen. The oxidation of cumene preferably occurs at a temperature between about 95°C and about 135°C. Overall, the first step can be illustrated as follows:



[0137] This reaction is a free-radical chain reaction. Oxygen initiates the reaction because it is a double free radical or diradical. In the initiation step, oxygen abstracts a hydrogen atom from cumene to give a resonance-stabilized benzylic free radical. Cumene hydroperoxide is formed in the subsequent propagation steps of the reaction. The cumene hydroperoxide then undergoes a rearrangement under acidic conditions to form phenol and acetone, as follows:



Preferably, the cumene hydroperoxide is treated with sulfuric acid, preferably with an about 5 to about 25 weight percent sulfuric acid solution, more preferably with an about 10 percent sulfuric acid solution. The rearrangement involves protonation of cumene hydroperoxide followed by loss of water to give an ion with an electron-deficient oxygen. This cation spontaneously rearranges to a more stable carbocation. The carbocation reacts with water to give form a hemiacetal

that is unstable and breaks down spontaneously to form the phenol and the acetone.

[0138] The reaction of cumene to acetone and/or phenol preferably occurs in a phenol/acetone synthesis unit. The first and second steps, illustrated and described above optionally both occur in the phenol/acetone synthesis unit or in separate reaction vessels.

[0139] Ideally, the acetone and phenol formed in the above reaction, in addition to any side reaction products, are separated in one or more separation units, e.g., distillation columns, extraction units and/or washing column. Exemplary side reaction products include acetophenone, 2-phenylpropan-2-ol and α -methylstyrene. Preferably, any α -methylstyrene produced is separated by vacuum distillation and hydrogenated back to cumene for recycle to the phenol/acetone synthesis unit.

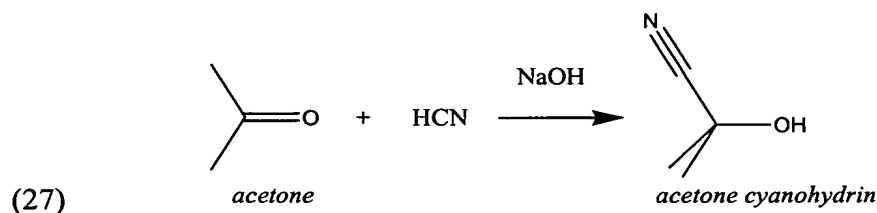
[0140] In one embodiment of the present invention, cumene formed from OTO-derived propylene is converted to phenol and/or acetone. The process includes providing a product stream containing propylene and an oxygenate contaminant. Preferably, the product stream is derived from an OTO reaction system, and more preferably from an MTO reaction system. The product stream is directed to a cumene derivative process reactor. In the cumene derivative process reactor, the propylene is converted to cumene. Preferably, the process includes contacting the propylene with an acid, preferably AlCl_3/HCl , sulfuric acid or hydrofluoric acid, under conditions effective to form cumene. The cumene then contacts an oxygen source, preferably molecular oxygen, under conditions effective to convert at least a portion of the cumene to cumene hydroperoxide. This conversion step optionally occurs in the cumene derivative process reactor or a separate cumene hydroperoxide synthesis unit. The cumene hydroperoxide preferably is directed to a phenol/acetone synthesis unit, which optionally is the same unit as the cumene derivative process reactor, the cumene hydroperoxide synthesis unit, or a third separate and independent synthesis unit. In the phenol/acetone synthesis unit, the cumene hydroperoxide preferably contacts an acid, preferably a 5-25% sulfuric acid solution, under conditions effective to convert at least a portion of the cumene hydroperoxide to one or both of phenol

and acetone. Preferably, both phenol and acetone are produced and subsequently separated in a separation unit, e.g., a distillation column.

Syntheses of Acetone Cyanohydrin and Methyl Methacrylate from Acetone

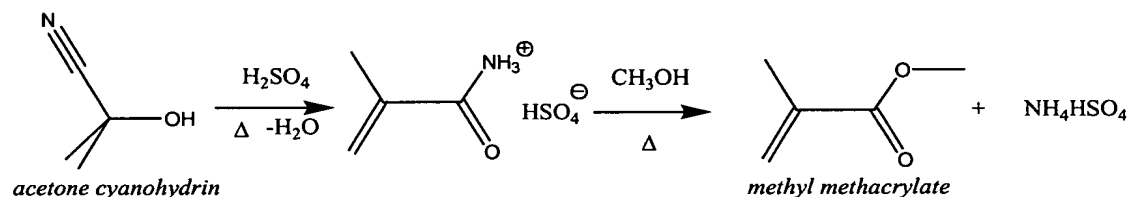
[0141] As indicated above, acetone is commercially valuable in the production of acetone cyanohydrin, Bisphenol A, methyl methacrylate (MMA), poly(methyl methacrylate) (PMMA) and as a solvent. Accordingly, the present invention is also directed to the production of acetone cyanohydrin, Bisphenol A, MMA, and PMMA from an OTO-derived propylene-containing feedstock.

[0142] Acetone cyanohydrin is synthesized through the nucleophilic addition of HCN to acetone in the presence of a base such as sodium hydroxide, as follows:



[0143] Dehydration of the alcohol group of acetone cyanohydrin followed by esterification with methanol synthesizes methyl methacrylate (MMA).

(28)



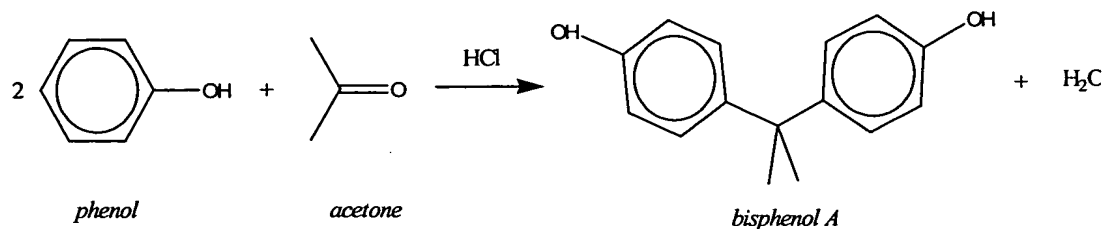
MMA is an extremely valuable monomer for the production of PMMA (approx. 1.2 billion pounds/year). PMMA is a high clarity resin used in glass substitutes.

Synthesis of Bisphenol A from Phenol and Acetone

[0144] Bisphenol A is manufactured from phenol and acetone. Bisphenol A is primarily used in the production of polycarbonate and epoxy resins. Polycarbonates are used as glass substitutes in the automotive, compact disc and

eyeglass industries. Without limiting the invention to a particular reaction mechanism, the reaction can be shown as follows:

(29)



The reaction preferably occurs at about 50°C. Typically, the reaction takes from about 8 to about 23 hours for maximum conversion. Some *ortho*, *para* isomers are formed, however, most of the product is *para*, *para*.

[0145] While the present invention has been described and illustrated by reference to particular embodiments, those of ordinary skill in the art will appreciate that the invention lends itself to variations not necessarily illustrated herein. For this reason, then, reference should be made solely to the appended claims for purposes of determining the true scope of the present invention.